

THE
LONDON EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

SEPTEMBER 1928.

XL. *The Direct Current Conductivity of Insulating Oils.*
By D. H. BLACK, Ph.D., M.Sc., *Research Laboratory*
of International Standard Electric Corporation *.

IT has long been known that, in general, when a difference of potential is applied across two electrodes immersed in a liquid dielectric, the current falls off with time, the rate of fall depending on various conditions. As distinct from most solid dielectrics this absorption current in oils is not reversible, and has been called the "irreversible anomalous current." Although the absorption effect is not reversible, there are in some cases traces of a small back-effect. These, however, are usually attributed to chemical polarization of the electrodes, and their effect can be allowed for when taking measurements.

The purpose of this paper is to give a simple theory which seems capable of explaining the observed phenomena, and to show how this theory is strongly supported by experimental evidence.

An absorption current can conceivably be caused in two ways: (1) a change in the resistance between the electrodes; and (2) the formation of polarization potentials due to an accumulation of charges in the dielectric—a kind of space-charge effect. From the irreversible nature of the absorption, and more particularly from the form of the current/time relationship observed on reversing the applied potential, it is considered that (2) above plays little, if any, part in the

* Communicated by Sir E. Rutherford, F.R.S.

phenomena. Reasons for this are given towards the end of the paper.

Assuming, then, that absorption is due to an increase of resistance, the question arises as to whether this increase is due to the building-up of a resistance at one, or both, of the electrodes ("contact resistance"), or whether it is due to the withdrawal of the conducting particles from the liquid itself. It is well known that conducting particles, especially water, can be removed from a liquid dielectric by the application of an electric field. These effects are, however, chiefly observed in more or less impure liquids. While it is not denied that a similar action may take place in reasonably pure dielectrics, it is here assumed that the predominating factor is the formation of a contact resistance.

The phenomenon of contact resistance has been observed by several workers when dealing with solid dielectrics*, and Hartshorn† put forward a theory to account for the usual absorption effects and power losses on these grounds. In the case of liquid dielectrics it seems to have been assumed that such contact effects are not encountered; but in the light of the present work this seems to be far from correct. Various workers have recorded the presence of a contact or transfer resistance with ordinary electrolytic solutions‡, and the action of the electrolytic rectifier is thought to depend on such an effect§. More recently Bryson||, when working with molten glass, observed a similar effect, the resistance being largely due to the formation of a gas layer at one electrode. Therefore, even without further experimental support, the assumption that a contact resistance is formed in liquid dielectrics seems quite justified.

Any building up of a contact layer at an electrode is most probably due to the transportation of material by the current flowing, the rate at which it is being formed being proportional to the current. It is observed that if a film of oil which has had a voltage applied to it for some length of time is short-circuited, the extra resistance which has been built up gradually disappears and the oil returns to its initial state. Thus it is evident that there is a force which is tending to remove this contact resistance, and this may be

* *E.g.* Joffé, *Ann. der Phys.* lxxii. 6, p. 461 (1923).

† *Proc. Phys. Soc.* vol. xxxvii. p. 215 (1925).

‡ See, for example, Newberry, *Roy. Soc. Proc. A*, cxi. p. 182 (1926); Crowther and Stephenson, *Phil. Mag.* vol. 1. p. 1066 (1925).

§ See Meserve, *Phys. Rev.* xxx. p. 215 (1927).

|| *Journ. Soc. Glass Techn.* xi. p. 331 (1927).

termed its tendency to recombine. From the analogy with the case of chemical mass action it is reasonable to assume that the rate of recombination is proportional to the magnitude of the resistance layer present.

Let R_0 be the initial resistance of the oil between the electrodes; R_s the final steady value of the resistance after the application of a potential E ; R the resistance at time t after the application of the potential; I_0 , I_s , and I the corresponding values of the current; and r the increase in the resistance. Then $R = R_0 + r$ and $R_s = R_0 + r_s$. Applying the assumptions made above, we get

$$dr/dt = kI - lr, \dots \dots \dots (1)$$

k and l being constants. When a steady value has been reached, $dr/dt = 0$, and so

$$r_s = kI_s/l;$$

hence
$$R_s = R_0 + nI_s, \dots \dots \dots (2)$$

where $n = k/l$. Therefore, if the values of R_s for different values of E are measured and graphed against the corresponding values of the current, the points should be on a straight line, cutting the axis $I = 0$ at the value of R_0 *.

Eliminating I by means of Ohm's law, we get

$$R_s = R_0/2 + \sqrt{nE + (R_0/2)^2} \dots \dots \dots (3)$$

If, by suitable switching arrangements, the time available for recombination is greater than the time the potential is applied, then the resistance ought to be decreased. A method is described later in which a commutator connected the potential across the film for a fraction of each revolution, the film being short-circuited for the remainder of the cycle. This was rotated at a speed which was sufficient for it to be assumed that the resistance remained constant throughout the cycle. If α is the fraction of one revolution during which the potential is applied, then

$$\frac{dr}{dt} = \alpha kI - lr, \dots \dots \dots (4)$$

and when $dr/dt = 0$,

$$R_s = R_0 + \alpha nI_s, \dots \dots \dots (5)$$

αI_s representing the average current flowing. Thus, while keeping the potential constant, values of R_s can be obtained

* It is of interest to note that Meserve (*loc. cit.*) obtains a similar relationship for the aluminium cell.

for different values of the average current by varying α . The relationship should still be linear.

If the absorption current observed in oils is due to the processes given above, then the value of R_0 obtained by varying the applied voltage should be the same as the initial value of the resistance obtained in taking an absorption curve, due allowance being made for the true capacity current. That is to say, both should give the true resistance of the oil itself. This has been found to be approximately correct in some cases; but in others the value of R_0 was found to be greater than the resistance observed fifteen seconds after the application of the voltage. The explanation suggests itself that R_0 is not the true resistance of the oil, but that there is a permanent contact effect at the electrodes which is independent of the passage of a current. The capacity and resistance effects of such a layer would conceivably give rise to absorption currents as outlined by Hartshorn*.

Whether R_0 is the true resistance of the oil or not, the values obtained for it by varying the thickness of the films by equal steps should differ by equal amounts. Also, since k and l would be expected to remain constant, the points obtained by graphing R_s against I_s should lie on a series of equidistant parallel lines.

If these deductions are correct, then on reversing the applied potential after the current had previously reached the steady state, the initial resistance would be the value of R_s before reversal†. The contact layer which had been built up at the one electrode would be removed while a similar one was being built up on the other. The rate of removal of the previously-formed layer would be greater than the rate of formation of the new one, since in the former case the current and the forces of recombination would be both tending to remove the layer. Such a state of affairs does not lend itself to simple mathematical treatment, but it is evident that one would expect the current to rise to a maximum and then fall off to the value of I_s before reversal.

So far, it has been assumed that a contact resistance is built up at one electrode only, but it is quite possible that one is formed at each electrode. It can easily be shown that in the latter case the relation between the resistance and the final current would still be linear. On reversing the applied potential, the rates at which the two films break

* *Loc. cit.*

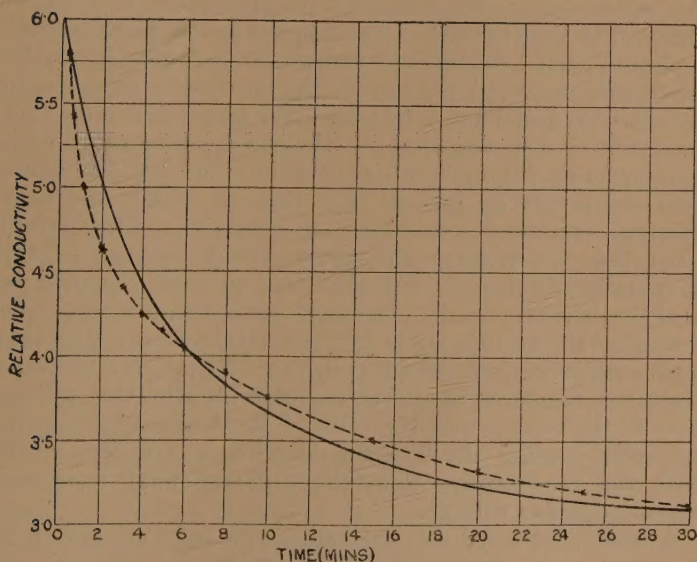
† The effect of the true capacity charges and discharges are not considered, as they would take place in a very small interval of time.

up might differ, and in that case one would expect to observe two maximum points. It is worth noting here that such a state of affairs is observed in some cases.

A comparatively simple equation connecting the resistance with the time of application of the potential can be found for the case in which a contact resistance is assumed to be built up at one electrode only, and the initial resistance is that of the oil itself. This is

$$t = -\frac{1}{l(R_s + r_s)} \left[R_s \log \frac{R_s - R}{r_s} + r_s \log \frac{R + r_s}{R_s} \right] \quad (6)$$

Fig. 1.



Theoretical absorption curve. (Broken curve shows initial part of fig. 7.)

Fig. 1 shows the form of the curve obtained for the relationship between conductivity and time when $R_s = 3.33$, $R_0 = 1.66$, and $l = 0.06$. The broken curve shows the experimental values obtained on an oil as shown in fig. 7. By suitably adjusting the undetermined constants R_0 and l , a closer agreement between the observed and calculated values could be obtained. It is, however, felt that the above simple case is the exception rather than the general rule, and that the mathematical complications involved if contact effects take place at both electrodes and

if permanent contact effects are present make exact comparison between calculated and observed values extremely difficult.

Most workers on the subject seem to be of the opinion that the conductivity of liquid dielectrics is electrolytic in character. If such is the case, then the liquid may be considered as an electrolyte of practically infinite dilution, so that "ionic" dissociation may be considered as being complete. The conductivity of an electrolyte is proportional to the number of ions present and to their mobility. If dissociation is complete the number of ions will not change with temperature, and the conductivity should vary in the same way as the mobility. That is to say, one would expect the resistance of the liquid to be proportional to the viscosity. This applies to the resistance of the liquid itself; but should resistances be built up at the electrodes, one would not expect the measured resistance to vary in such a manner. It seems reasonable to assume that the value of k in equation (1) would not vary greatly with temperature; but one would expect the value of l to increase with temperature, just as the rate at which ordinary chemical reactions are known to increase. This would mean that the relative absorption would decrease as the temperature increased, and that the ratio of viscosity to final resistance would increase with temperature, the viscosity/temperature curve being much less steep than that for the resistance/temperature relation. Also, the value of the resistance measured at short time intervals after the application of the voltage and the value of R_0 obtained by varying the voltage across the film should change at a slower rate with the temperature than the ordinary final resistance measured under voltage.

It should be noted that the values of k and l are not to be expected to be similar for different liquids. In general it seems that for oils the greater the resistance of the oil itself the greater the value of the contact resistance built up for any given voltage. Thus the value of l seems to depend on the conductivity in such a way that the more ions there are present in the liquid the greater the tendency for the contact resistance to recombine. The reasons for this are not evident, but they may be connected with the results to be mentioned later dealing with the addition of moisture to oils. However, it is interesting to note that Crowther and Stephenson* observed a similar effect in ordinary electrolytes.

* *Loc. cit.*

Experimental.

The theory put forward above was developed from the consideration of experimental results obtained from insulating oils. The work, which is still in progress, was undertaken with a view to attempting to discover the fundamental nature of the electrical conductivity of liquid dielectrics. A great deal of time has been taken up in overcoming experimental difficulties, a description of which is too lengthy to be included here; and, so far, the results obtained have been mainly concerned with what may be termed the "anomalous effects" rather than with the conductivity of the oils themselves.

The oil under test was contained in a conical vessel forming one electrode and having an inner concentric electrode which was guarded at top and bottom. The vessel was sealed off from the atmosphere by means of two ground joints, and it was capable of being evacuated to comparatively low pressures. The film thickness could be accurately varied without opening the vessel in any way. The vessel and electrodes were constructed of brass, using bakelite for the necessary insulation, and the actual surfaces exposed to the oil were tinned to lessen any tendency to form sludge. The testing vessel was placed in an electrically-heated oven, the temperature of which could be regulated to keep the temperature of the oil film constant to within $0.1^{\circ}\text{C}.$, and by taking particular care the variations could be kept to $0.02^{\circ}\text{C}.$ In general the resistance of the oil was measured by direct deflexion methods, using a sensitive moving-coil galvanometer*.

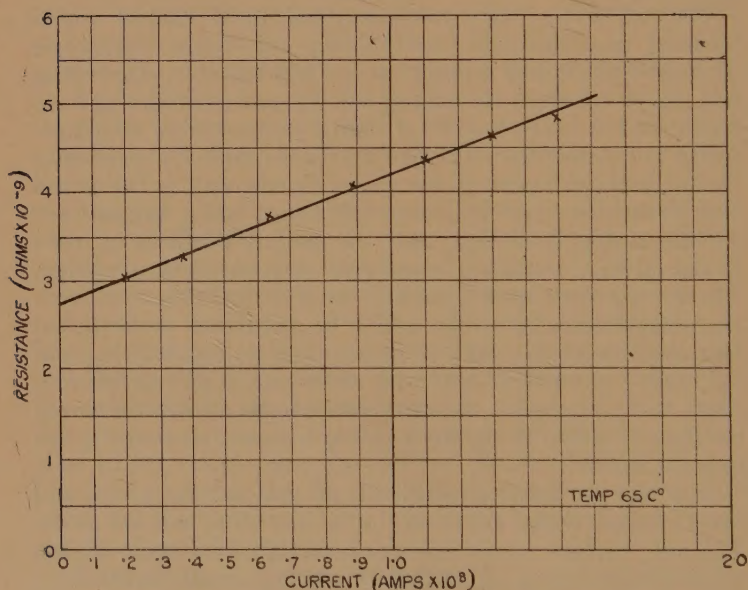
The liquids used were all oils of the paraffin series, and these were usually supplied in a carefully purified state. The only further treatment they received was vacuum drying when in the testing apparatus, this being usually carried out at a temperature of $60^{\circ}\text{C}.$ – $70^{\circ}\text{C}.$ The idea may be advanced that the vagueness of the constitution of the oils used detracts from the scientific value of the results; but it is very difficult to obtain liquids whose chemical constitution is definitely known and which are of sufficiently high resistivity to be considered as insulators. Moreover, since the effects studied do not deal with the nature of the oils themselves, but with

* It is obviously important to be able to measure the resistance of the oil films at very short intervals after the application of the potential. So far it has not been possible to do this, but it is hoped that a string galvanometer will be available in the near future when such observations will be attempted.

the electrode phenomena, it is thought that the constitution of the oils is, in the present case, of secondary importance.

Fig. 2 shows the straight-line relation between current and resistance for medicinal paraffin oil, and fig. 3 shows the same for a thin engine oil taken at several film thicknesses *. The curves were taken by varying the voltage in steps and leaving an interval of one hour at each change of voltage before taking a reading. In the latter case it will be observed that the points line on a series of equidistant parallel straight lines as indicated by the theory.

Fig. 2.

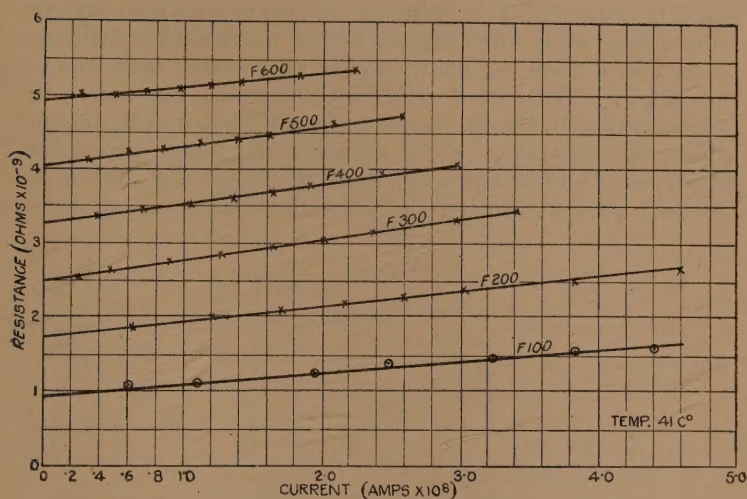


Relation between resistance and current for paraffin oil.

Fig. 4 is a diagram of the method used for increasing the proportion of the time of recombination to the time of current flow. The commutator consisted of a piece of heavy copper tubing, about 7 inches long and 3 inches in diameter, which was divided in two by a diagonal saw-cut. The two halves were mounted on a wooden cylinder supported on ball bearings. Two fixed brushes made contact with the two

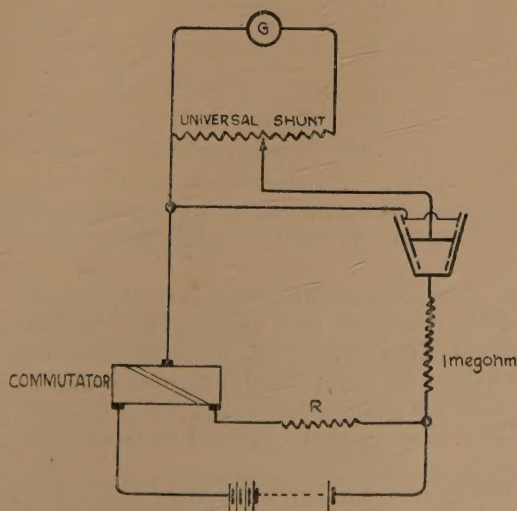
* The film thicknesses, when given, are expressed in divisions of the rotating head which varied the distance between the electrodes. The head was divided into 100 divisions, and 646 divisions on the head corresponded to 0.1 inch film thickness.

Fig. 3.



Relation between resistance and current for an engine oil.

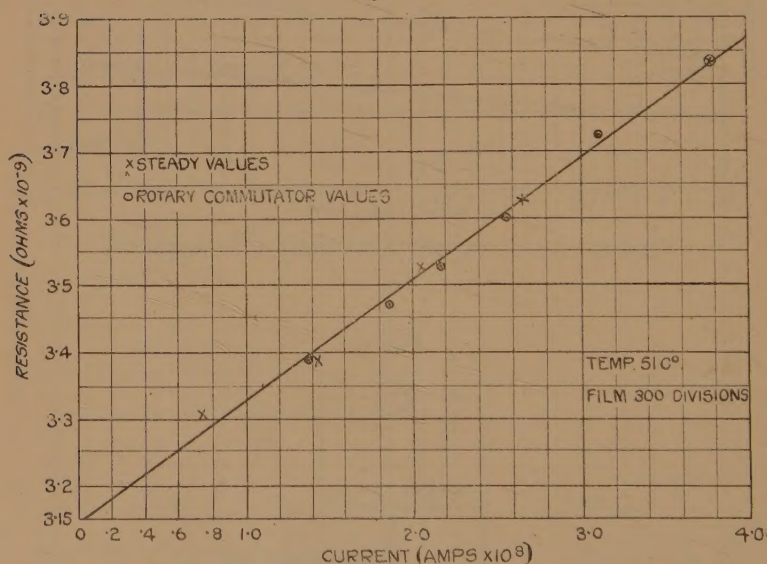
Fig. 4.



Connexions for rotary commutator.

segments, and a third brush could be adjusted so that the proportion of each segment which came into contact with it could be altered. The resistance R prevented the battery from being short-circuited while the movable brush made contact with both segments at once as it passed from one to the other. The value of R , 50,000 ohms, was small in comparison with the resistance of the oil film, and so did not affect the readings. Pure capacity and other reversible effects were eliminated, since both the charge and discharge currents passed through the galvanometer, but in opposite

Fig. 5.



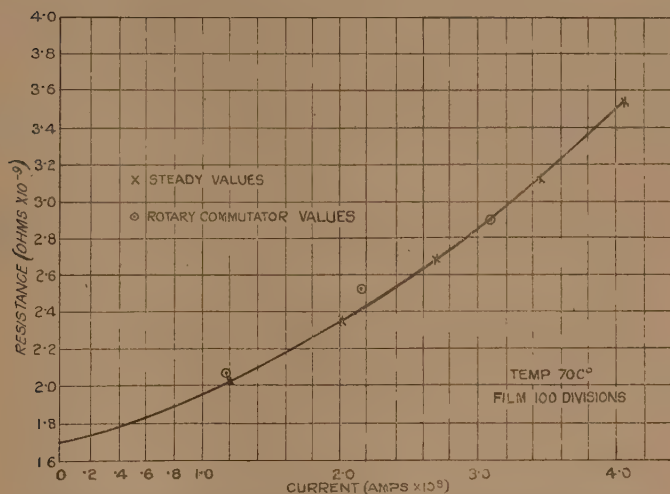
Showing agreement between values of resistance obtained by varying the voltage and by means of the rotary commutator.

directions. The commutator was run at a speed of from 1000 to 1200 revolutions per minute, and this gave a steady galvanometer deflexion. The method of obtaining the resistance values was quite straightforward, and fig. 4 shows that the resistance graphed against average current gives the same straight line as that obtained by varying the applied voltage.

While the general tendency seems to be for the resistance to have a linear relationship with the current flowing, yet such a simple state of affairs does not always exist. This is especially so in the case of freshly-prepared oil films, and

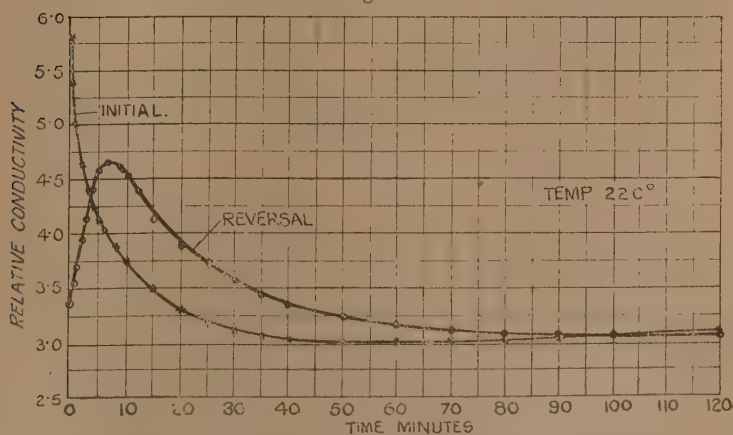
fig. 6 shows the resistance/current relationship for the same sample of oil as in fig. 5, but taken soon after the oil was introduced into the tester and also at different temperature and film thickness. It will be observed, however, that the

Fig. 6.



Showing non-linear relationship between resistance and current.

Fig. 7.



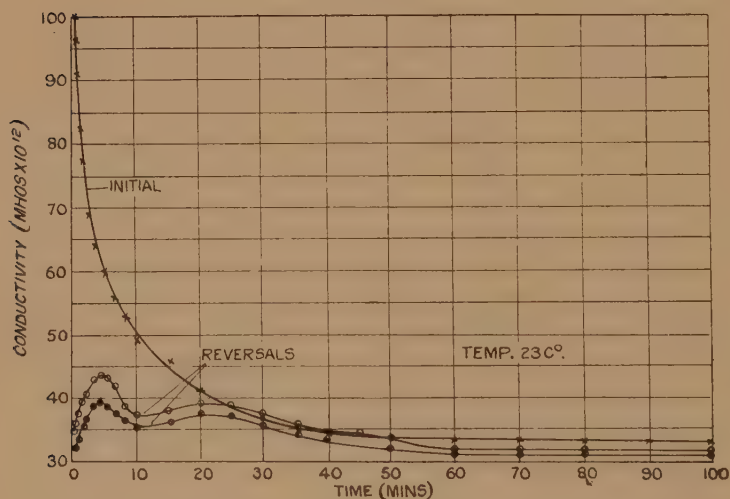
Relation between conductivity and time for transformer oil.

resistance values obtained by means of the rotary commutator lie approximately on the same curve as those obtained by varying the voltage.

Fig. 7 shows a typical absorption and reversal curve, the liquid being a transformer oil. It will be noticed that the curve obtained on reversal rises to a maximum and then falls away as indicated *. Fig. 8 is a similar curve showing the double maxima sometimes obtained on reversing the applied potential.

The resistance of an oil film sometimes varies according to the direction in which the current is flowing. This is easily explained by the theory, since the two electrodes may not have exactly similar surfaces, thus altering the values of k and l . This accounts for the fact that the two reversal

Fig. 8.



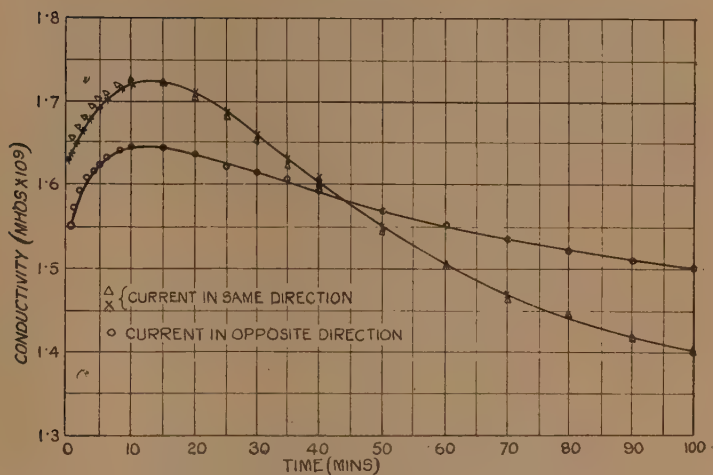
Conductivity-time curves showing double maxima on reversal.

curves in fig. 8 are not coincident. The phenomenon is shown more definitely in fig. 9. Curve I. shows the relationship with the current in one direction, and curve II. that with the current reversed. On reversing the current a second time the points obtained lie on curve I. once more.

Fig. 10 shows the ratio of viscosity to final resistance for medicinal paraffin. The points are plotted on a logarithmic scale for the sake of convenience. The fact that the resulting graph is a straight line may be of importance, but

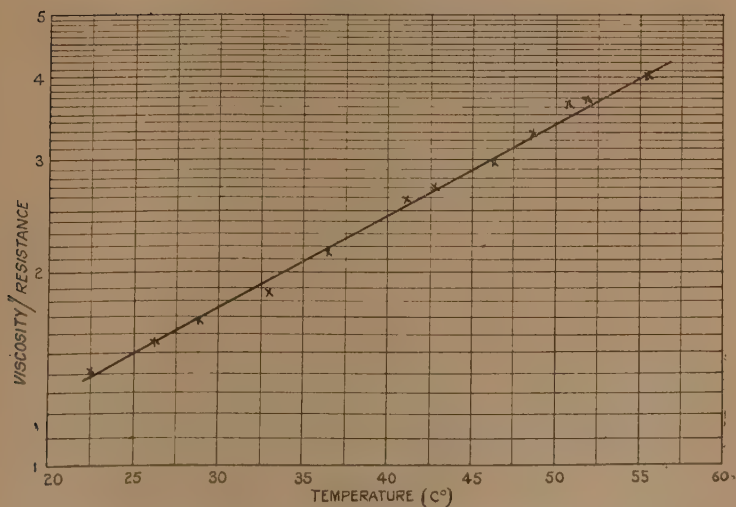
* Similar curves have been obtained for liquid bromine (Anderson, Phys. Soc. Proc. xl. p. 62, 1928) and for liquid sulphur (Black, Proc. Camb. Phil. Soc. xxii. p. 393, 1924).

Fig. 9.



Variation of conductivity with direction of current (transformer oil).

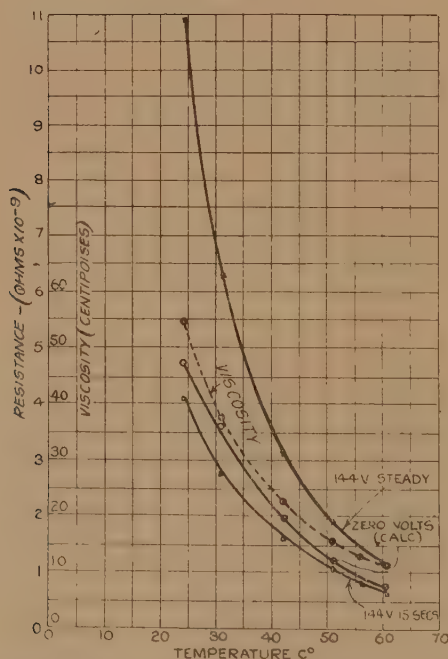
Fig. 10.



Variation of the ratio of viscosity to resistance with temperature (paraffin oil).

the main fact to notice here is that the resistance decreases much more rapidly than the viscosity. Fig. 11 shows the difference in the rate of change of resistance with temperature of an oil film of 0.46 inch thickness when measured 15 seconds after the application of the voltage and after a steady deflexion had been obtained; and in addition the values of R_0 obtained from the resistance/current relationships are shown for the different temperatures. It will be noticed

Fig. 11.



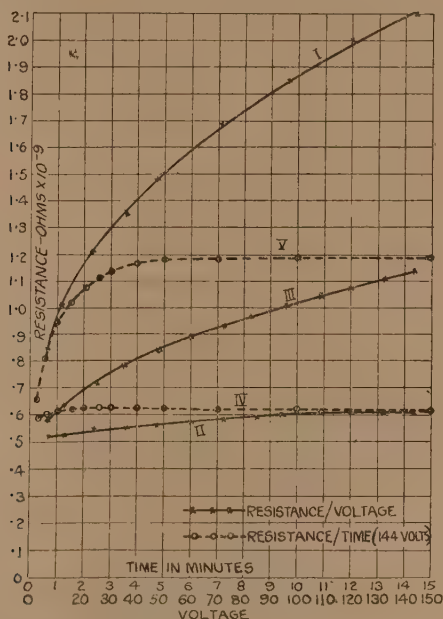
Effect of temperature on resistance and viscosity of on engine oil.

that the resistances measured after 15 seconds are less than the values of R_0 in each case, suggesting the presence of a contact resistance before the application of any voltage. The viscosity/temperature curve is seen to be more nearly parallel to the lower curves than to that obtained for steady values of resistance at 144 volts.

Some experiments have been made in an attempt to determine the effect of moisture on the resistance of an oil, and some of the results are of interest in the light of the

present theory. Moisture was brought into contact with the oil in the form of water vapour, at the same temperature as the oil, by connecting a small flask of water to the testing apparatus. The amounts absorbed were very small, and it was not found practicable to measure them with an ordinary chemical balance. In fig. 12, curve I. shows the resistance/voltage relationship before exposure to moisture, curve II. the same after 60 hours' exposure to moisture, and curve III. after 16 hours' vacuum drying after the exposure.

Fig. 12.



Showing effect of moisture on transformer oil (temp. 60° C.).

Curves IV. and V. show the resistance/time relationships at 144 volts corresponding to curves II. and III. respectively. The main effect of the moisture seems to be to reduce the value of the contact resistance built up without changing the resistance of the oil to any great extent, since all the five curves appear to cut the ordinate at approximately the same point.

It may be asserted that the above phenomena could also be explained by the assumption that space charges are set up in liquid dielectrics. However, this seems to be negated

by two main facts :—(1) The absorption curve of an oil may take some hours to reach a steady value. If this were due to the gradual formation of a space charge, one would expect that, on removing the applied voltage and short-circuiting the film, the charge would take a similar length of time to disappear, and would give a residual current/time curve comparable with the original absorption curve. Such is not observed in oils. (2) If a space charge is built up giving an opposing E.M.F., then on reversing the applied potential this space effect should be acting in the same direction, giving a larger current than that observed at the beginning of the original absorption curve. That such is certainly not the case is indicated by the reversal curves shown.

No mention has so far been made of the probable nature of the contact resistance. There is a certain amount of evidence to suggest that it exists in the form of a gas layer on one or both electrodes; but until further experimental support is obtained it must be regarded as a tentative suggestion only.

Finally, it should be pointed out that, when a contact resistance is built up, the layer so formed may have a large capacity, and thus, when the final steady current has been attained, the combination of oil and contact layer may act as an ordinary two-layer dielectric, following ordinary Maxwellian theory. In the case of ordinary insulating oils, however, the residual effects so obtained would be small in comparison with the change in the resistance of the contact layer. It is conceivable that such an effect might be detected with an oil of very high specific resistance.

Summary.

A theory is put forward to account for the absorption current in liquid dielectrics. It is assumed that contact resistances are formed at one or both electrodes by the passage of an electric current, this causing the well-known decay of current with the time the potential has been applied across the electrodes. Experimental support of the theory is given, and it seems capable of explaining in a simple manner the anomalous conductivity phenomena observed in liquid dielectrics under D.C. stresses.

My thanks are due to the International Standard Electric Corporation for permission to publish these results.

I am also indebted to Mr. J. D. Cockcroft of the Cavendish Laboratory for much helpful criticism.

XLI. *The Action of X-Rays on Colloidal Ceric Hydroxide.*
By J. A. V. FAIRBROTHER, B.Sc.*

INTRODUCTION.

IN a previous joint paper with Professor Crowther† we reported upon the action of X-rays on colloidal Iron, Copper, Silver, and Gold. It appeared that cationic sols, that is, sols in which the particles are attracted towards a negative pole, are coagulated, whilst anionic sols become more stable. Since then we have irradiated many more positive and negative sols and have found no exception to this rule. From the numerical investigation of a Bredig copper sol, it was suggested that coagulation was due to the destruction of the electrokinetic potential by ionization produced by the rays in the diffuse double layer surrounding the particles.

By measuring the viscosity changes produced in a viscous sol by X-rays, it was hoped to study and follow the changes taking place in the electrical state of the particles. The researches described in this paper were undertaken with this end in view.

Smoluchowski has developed the following formula for the viscosity of a colloidal solution :

$$\mu_s = \mu_w \left\{ 1 + 2.5 \phi \left[1 + \frac{1}{\lambda \mu_w r^2} \left(\frac{D\xi}{2\pi} \right)^2 \right] \right\} .$$

μ_s and μ_w are the viscosities of the sol and water respectively.

ϕ is the volume of the particles in unit volume of the solution.

r is the mean radius of the particles.

λ the specific conductivity of the sol.

D the dielectric constant.

ξ the electrokinetic potential.

If it be assumed that ϕ , λ , and r remain constant, we can deduce a very simple relation between the viscosity of the sol and the electrical charge on the particles.

For

$$\frac{\mu_s}{\mu_w} = 1 + 2.5 \phi + K \xi^2,$$

where K is a constant.

* Communicated by Professor J. A. Crowther, Sc.D.

† Crowther & Fairbrother, *Phil. Mag.* iv. August 1927.

If μ_{s0} is the viscosity of the sol when the electrokinetic potential on the particles is destroyed, then

$$\frac{\mu_{s0}}{\mu_w} = 1 + 2.5 \phi. \quad (1)$$

$$\therefore \frac{\mu_s}{\mu_w} - \frac{\mu_{s0}}{\mu_w} = K \zeta^2.$$

Now q , the charge on a particle, is proportional to ζ . It will also be proportional to $X - x$, where X is the X-ray dose required to discharge the particle completely, and x the dose which it has actually received.

Therefore

$$\frac{\mu_s}{\mu_w} - \frac{\mu_{s0}}{\mu_w} \propto (X - x)^2. \quad (2)$$

We may conclude

- (1) That the curves obtained by plotting $\frac{\mu_s}{\mu_w}$ against x , the X-ray dose applied, should be parabolic in form.
- (2) That when all the particles have been discharged, the viscosity should be given by formula (1) above.

This formula is the one developed by Einstein relating the viscosity of a sol to the number of particles in unit volume, a formula in which no account is taken of the electrokinetic potential. If ϕ is small so that 2.5ϕ is negligible compared with unity, then

$$\mu_{s0} = \mu_w,$$

and the viscosity of the sol should equal that of water.

Fernau and Pauli* have coagulated a positive ceric hydroxide hydrosol and denatured albumen with the rays from radium. This second observation has been repeated with X-rays†. In the case of ceric hydroxide hydrosol, they observed that the viscosity first decreased to a minimum, then rose rapidly, and that the sol finally set to a gel. This particular sol appeared well suited for such a research as we had in mind. Preliminary investigation showed it to be very susceptible to X-rays and to give marked viscous changes with varying doses.

* Fernau & Pauli, *Kolloid. Zeit.* xx. p. 20 (1917); *ibid.* xxx. p. 6 (1922).

† Fairbrother, 'British Journal of Radiology,' April 1928.

EXPERIMENTAL DETAILS.

The experimental arrangements were similar to those described in the previous paper.

The source of radiation was a Shearer tube with a molybdenum anticathode, run at a P.D. of 55,000 volts and a current of 4 m.a. by means of a large induction coil and mercury break. The resultant beam consisted largely of molybdenum K-radiation with a mean coefficient of absorption in aluminium of 4.6.

The liquid to be exposed was contained in a small quartz boat 28 mm. by 9 mm. and 9 mm. deep. The beam completely filled the dish. 1 c.c. of liquid was always exposed, and filled the dish to a depth of 5 mm. An equal volume of the sol was placed in a similar dish and treated in exactly the same way. Both the exposed and control samples were sealed down under boxes, the tops of which were closed with thin glass cover-slips 0.2 mm. thick. By thus hermetically sealing the liquids, any changes brought about by exposure to the atmosphere were eliminated, and by comparing the exposed sample directly with the control, any changes brought about in the actual sealing process were eliminated also.

The viscosimeter consisted simply of a vertical capillary tube with an intermediate bulb of 1 c.c. capacity and a reservoir at the base. The liquid was sucked up from the reservoir, and the time taken for it to fall from a mark on the capillary above to a mark on the capillary below the bulb gave a measure of the viscosity. The instrument stood in a thermostat kept constantly at 20° C. The difference between the times taken by the exposed and control samples divided by the control time clearly gives the fractional change in viscosity. In these experiments the control time remained so constant that it was quite safe to assume that the changes in the exposed sample were due entirely to the radiation.

The intensity of the radiation was measured by means of an air-gap ionization chamber, so constructed that the volume of ionized gas between the plates was 1 c.c. A standard 1 mf. condenser was connected to the insulated plate of the chamber, and the radiation necessary to charge the condenser to a P.D. of 1 volt was taken as the unit of dosage, and will be referred to as a microcoulomb, or 1 mc. A dose of 1 mc. corresponds to a dose of 3000 e in the ionization chamber, where e is Friedrich's unit of dosage.

The window of the chamber was distant 10.75 cm. from

the focal spot of the tube. If the surface of the liquid is distant x cm. from the focal spot, the dose given to the exposed sample is $\left(\frac{10.75}{x}\right)^2$ mc. The time taken to apply a unit dose varied with the condition of the tube, but was usually about 20 minutes. In all sets of readings different doses were applied to the sol by varying the distance of the surface of the exposed sample from the focal spot. The dose measured in the ionization chamber was the same throughout any set of readings, so that the time taken to apply different doses was constant.

PREPARATION OF THE SOL.

About 5 gm. of ceric ammonium nitrate crystals were dissolved in 50 c.c. of distilled water. The solution was immediately poured into a glass bell-shaped dialyser covered with stiff parchment, and the whole stood in a dish of distilled water. Two factors are essential for successful preparation. First, dialysis must take place as uniformly as possible throughout the sol. This is ensured by using a large membrane surface. Secondly, the dialysis must be slow. For this reason, rather than remove the dialysate with a stream of running water, the dialyser stood in a dish of distilled water, which was removed every four or six hours. Under these conditions and after about three days a beautiful lemon-coloured viscous sol of ceric hydroxide is obtained. If this is now stored in a hard glass or quartz flask, a spontaneous increase in viscosity ensues, and the liquid eventually sets to a clear stiff gel. If this stock is diluted before gelling takes place, the viscosity continues to increase, though less rapidly, and by repeating the dilution a sol is obtained which is quite thick, and the viscosity of which may be considered to remain sensibly constant for a number of hours.

RESULTS.

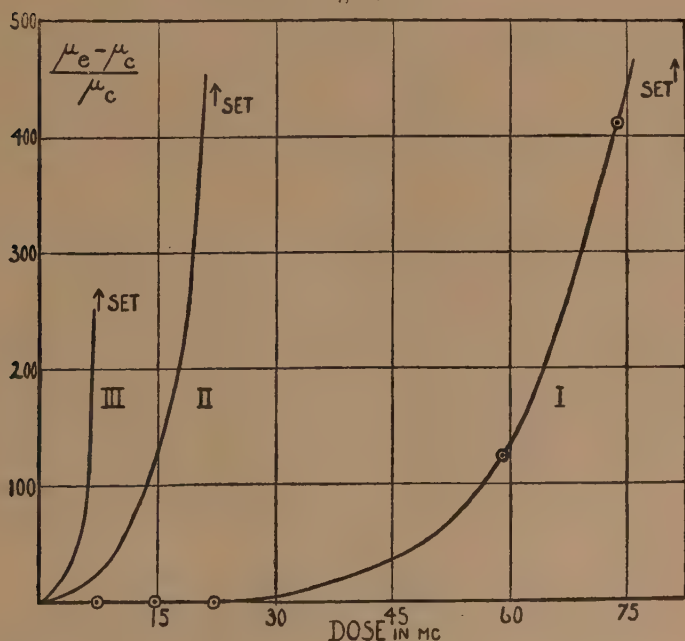
A. *Susceptibility of the sol to X-rays with ageing.* (Figs. 1 & 2.)

A solution of 5 gm. of ceric ammonium nitrate in 50 c.c. of distilled water was dialysed from November 26th to 29th, and the resultant sol stored in a quartz flask. When irradiated, it showed an increase in viscosity, the rate of increase becoming rapidly larger with increasing doses. Finally, the sol set to a gel. A similar viscosity increase takes place with age although two or more weeks elapse before the sol

sets. If μ_e and μ_c represent the viscosities of the exposed and control samples respectively, then $\frac{\mu_e - \mu_c}{\mu_c}$ is the percentage change in viscosity. In fig. 1 are plotted values of $\frac{\mu_e - \mu_c}{\mu_c}$ against the corresponding X-ray doses for the same sol on three different days.

Curve I. was taken on December 1st, three days after completion of dialysis. Initially, the viscosity increase is

Fig. 1.



very small. It then increases rapidly and the sol gels with a dose of 81.1 mc.

The behaviour of the same sol on December 5th and 6th is given in curves II. and III. respectively. On December 5th it was set to a gel by a dose of 22.1 mc., and on December 6th by 7.4 mc. Thus, as the sol ages, its viscosity continually increasing, it becomes very much more sensitive to X-rays. The water value of the viscosimeter used was 7.2 seconds, and the control times on the three days December 1st, 5th, and 6th were 8.0, 10.3, and 11.0 seconds. If μ_w denotes the water value of the viscosimeter, then $\frac{\mu_c - \mu_w}{\mu_w}$ is the

percentage excess of the viscosity of the control over that of water. Throughout the experiments there was never found any appreciable difference between the viscosities of the stock sol and the control, so that the control time may be taken to mean as well the stock time.

The data for these curves are collected in Table I.

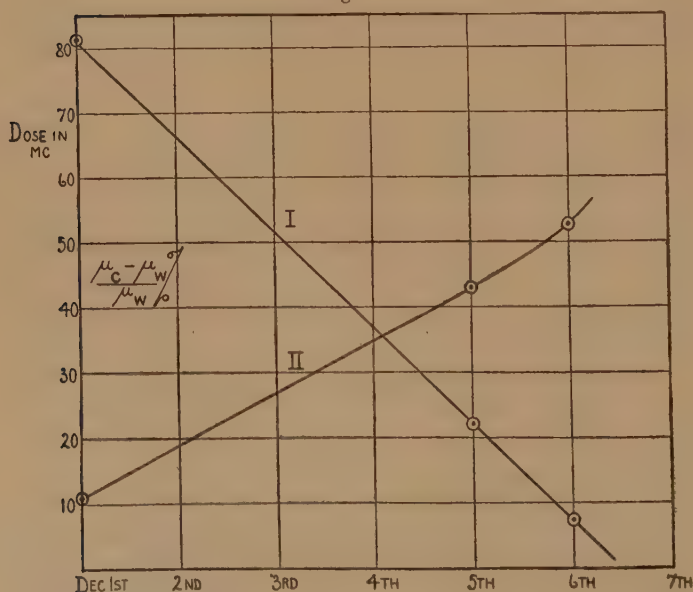
TABLE I.

Control time (seconds).	Date.	Gelling dose. (mc.).	$\frac{\mu_c - \mu_w}{\mu_w}$ %.
8.0	Dec. 1st	81.1	11.1
10.3	Dec. 5th	22.1	43.0
11.0	Dec. 6th	7.4	52.8

Time taken to apply to each dose = 40 minutes.

Water value of the viscosimeter = 7.2 seconds.

Fig. 2.



The straight line I. in fig. 2 is obtained by plotting the dose required to set the sol to a gel against the days. The fact that this dose decreases linearly with time suggests that the ageing effect and the action of the radiation are additive.

In curve II. $\frac{\mu_c - \mu_w}{\mu_w}$ is plotted against the time. The relation is almost a linear one over the period studied, but the curve begins to curve upwards, and would continue to do so more and more rapidly until finally the sol gelled.

B. *Change in viscosity produced by the rays in sols of different concentrations.* (Figs. 3 & 4.)

Portions of a fresh and rather viscous stock sol were diluted with distilled water to give solutions of one-half, one-third, one-quarter, and one-eighth the concentration. If the strength of the stock sol made by dialysing a solution of 5 gm. of ceric ammonium nitrate in 50 c.c. of water is denoted by S, then the concentrations of these new sols can be represented by $\frac{S}{2}$, $\frac{S}{3}$, $\frac{S}{4}$, and $\frac{S}{8}$. Samples of these sols were placed with the surface of the liquid distant 2.8 cm. from the focus of the tube, and a dose of 1 mc., as measured in the ionization chamber, given to each. Since the distance of the chamber window from the focal spot on the tube was 10.75 cm., the dose actually incident upon the surface of the liquid exposed was $\left(\frac{10.75}{2.8}\right)^2 = 14.75$ mc. This was the same for each sample. The percentage change in viscosity $\frac{\mu_e - \mu_c}{\mu_c}$ produced by this dose in each solution was plotted against the concentration. The resultant curve is given in fig. 3 and the data in Table II.

TABLE II.

Concentration.	μ_c (seconds).	μ_e (seconds).	$\frac{\mu_e - \mu_c}{\mu_c}$ %.
$\frac{S}{2}$	65.3	77.2	+18.3
$\frac{S}{3}$	34.9	36.2	+ 3.8
$\frac{S}{4}$	27.1	26.2	- 3.5
$\frac{S}{8}$	19.8	19.0	- 3.8

Water value of viscosimeter = 10.5 seconds.

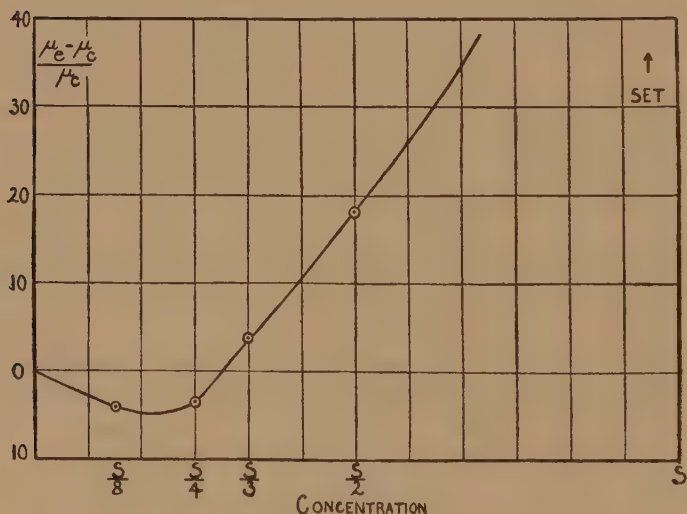
X-ray dose given = 14.75 mc.

Time taken to apply the dose = 20 minutes.

Sols of low concentration show quite a marked decrease in viscosity with a dose of 14.75 mc., whereas the stock solution from which the more dilute ones were prepared is set to a gel by the same dose.

In fig. 4 $\frac{\mu_{\text{exposed}}}{\mu_{\text{water}}}$ is plotted against varying X-ray doses for sols one-third, one-fourth, and one-sixth the stock concentration. These sols are denoted by $\frac{S}{3}$, $\frac{S}{4}$, and $\frac{S}{6}$. Each one was made on the day of investigation by diluting a portion of the same stock. Curves I. and IV. apply to the

Fig. 3.



sol of $\frac{S}{4}$, but curve IV. was taken two weeks after curve I.

The data for the curves of fig. 4 are set out in Table III.

According to the theory discussed in the introduction to this paper we should expect the curves obtained by plotting

$\frac{\mu_{\text{exposed}}}{\mu_{\text{water}}}$ against the X-ray dose to be parabolic in form. Instead, the value of $\frac{\mu_{\text{ex}}}{\mu_{\text{w}}}$ decreases rapidly at first and then

gradually approaches a limiting value. In the case of Curves I., II., and III. the limiting value is almost equal to unity, whilst that of curve IV. is not greater than 1.25.

TABLE III.

Distance of liquid surface from focus.	I.		II.		III.		IV.	
	$\frac{S}{4}$ Jan. 24th.		$\frac{S}{6}$ Jan. 26th.		$\frac{S}{3}$ Jan. 27th.		$\frac{S}{4}$ Feb. 6th.	
	μ exposed (seconds).	$\frac{\mu \text{ exposed}}{\mu \text{ water}}$	μ ex.	$\frac{\mu \text{ ex.}}{\mu \text{ w.}}$	μ ex.	$\frac{\mu \text{ ex.}}{\mu \text{ w.}}$	μ ex.	$\frac{\mu \text{ ex.}}{\mu \text{ w.}}$
*	—	0	17.30	1.697	15.39	1.510	25.72	2.521
6.30	—	2.99	—	—	11.40	1.118	—	—
5.30	—	8.24	13.14	1.289	10.40	1.020	16.10	1.579
3.30	—	21.26	10.75	1.054	10.21	1.091	11.91	1.168
2.80	—	29.50	10.73	1.052	10.22	1.002	11.43	1.122
2.30	—	43.62	10.35	1.015	11.27	1.104	13.87	1.360
1.88	—	65.43	11.87	1.163	13.68	1.340	gelled	∞
† 2.3	—	87.24	30.96	3.018	18.90	1.854	—	—

Distance of ionization chamber window from the focus of the X-ray tube = 10.75 cm.

Water value of viscosimeter = 10.20 seconds.

Time taken to apply each dose = 30 minutes.

* Along this line μ exposed = μ control, the control time.

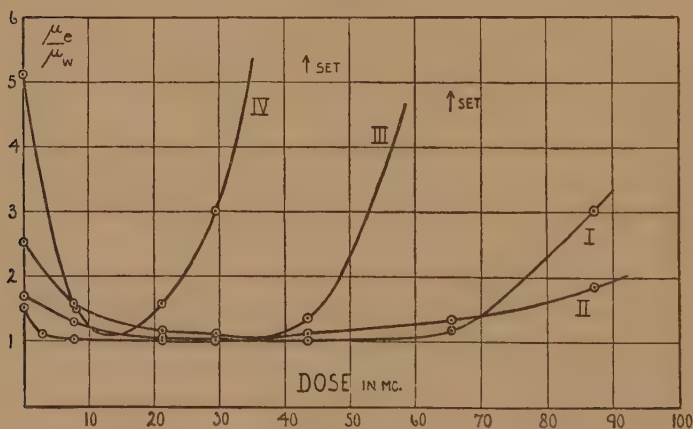
† Time taken to apply this dose = 60 minutes.

Table IV. gives the approximate dose, as deduced from the curves of fig. 4, necessary to produce the maximum decrease in viscosity in each of the sols investigated, and the date on which each curve was obtained.

TABLE IV.

	I.	II.	III.	IV.
	Jan. 24th.	Jan. 26th.	Jan. 27th.	Feb. 6th.
Dose in mc. producing maximum decrease in viscosity	45	33	35	13
Concentration	$\frac{8}{4}$	$\frac{8}{6}$	$\frac{8}{3}$	$\frac{8}{4}$

Fig. 4.



If we regard the difference between the doses producing the maximum decrease in curves II. and III. as being insignificant, the difference lying within the limit of the error in reading the minimum points on the curves, then we can say that the dose required to produce the maximum lowering of the viscosity decreases with the age of the stock sol from which each of the solutions were made. This is in agreement with the observations made in Section A.

The fact that the curves are not parabolic must be due to a variation of one of the factors ϕ , λ , and r the mean radius of the particles, which, in the theory, were assumed to remain constant. Experiments described in Section C showed that

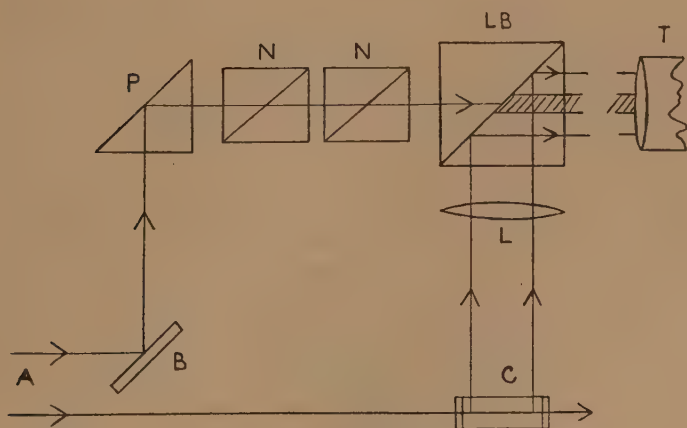
the mean radius of the particles was decreasing up to the position of minimum viscosity.

C. *Change in size of the particles with varying doses of X-rays.* (Figs. 5 & 6.)

In order to study the changes, if any, in the average size of the particles, use was made of the Tyndall meter, an instrument devised by Mecklenburg for comparing the intensities of two beams of light.

A parallel beam of light A (fig. 5), in this case a pointolite projected with Zeiss projecting apparatus, is allowed to pass

Fig. 5.

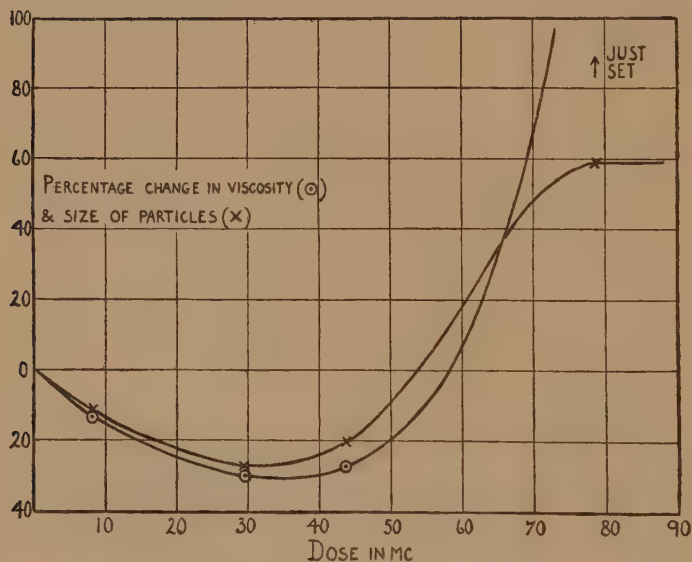


through the solution contained in a cylindrical glass tube C, closed at the ends with thin plate-glass. Half of the beam is diffusely reflected upwards by means of a plaster-of-paris slab B, and again made parallel to the original beam by means of a right-angled prism P. This beam then passes through two Nicol prisms NN and through the central spot of a Lummer-Brodhun cube LB, into the telescope T. The light scattered in the tube C is collected by the lens L and reflected as a parallel beam into the telescope. By rotating one of the nicols, the intensity of the upper beam can be cut down until equal to the lower, in which case a uniform field is seen in the telescope, the central spot disappearing entirely. The intensity of the upper beam is reduced by suitable filters until it is nearly equal to that of the beam of scattered light. In this case the principal planes of the

nicols make an angle of about 45° with one another when a uniform field is seen in the telescope and the accuracy of comparison of the beam is then a maximum. If θ_1 and θ_2 are the angles between the principal planes of the nicols for beams of intensities J_1 and J_2 when a uniform field is seen in the telescope, then

$$\frac{J_1}{J_2} = \frac{\cos \theta_1}{\cos \theta_2}.$$

Fig. 6.



The intensity of light scattered is given by

$$J \propto \frac{nv^2}{\lambda^4}.$$

n is the number of particles per c.c.

v^2 the mean of the squares of the volumes of the particles.

λ the wave-length of the incident light.

The concentration c of the sol is

$$c = n \cdot v \cdot \rho,$$

where ρ is the density of the particles, and for the same sol c remains constant, so that we may write

$$J_1 \propto \frac{v_1 c}{\lambda^4 \rho}, \quad J_2 \propto \frac{v_2 c}{\lambda^4 \rho}.$$

$$\therefore \frac{J_1}{J_2} = \frac{v_1}{v_2} = \frac{\cos \theta_1}{\cos \theta_2}.$$

In fig. 6 the percentage change in the average size of the particles and the percentage change in viscosity of the sol, which, in this case was one-fourth the concentration of the usual stock solution, are plotted against the X-ray doses. The data are given in Table V. It is rather surprising that the percentage decrease in the size of the particles from the origin to the minimum viscosity point is proportional, and, in fact, almost equal, to the fractional change in viscosity. After the minimum point is reached gelling sets in, and the particles show a maximum increase of about one and a half times their normal size.

TABLE V.

Distance of liquid surface from focal spot. (cm.)	Dose (mc.).	μ exposed (seconds).	μ control (seconds).	$\frac{\mu_{\text{ex.}} - \mu_{\text{con.}}}{\mu_{\text{con.}}} \%$	$\theta_{\text{ex.}}$	$\theta_{\text{con.}}$	$\frac{\cos \theta_{\text{ex.}}}{\cos \theta_{\text{con.}}}$	Percentage change in size of particles.
5.3	8.2	20.8	24.0	-13.3	61.3°	57.5°	.895	-11
2.8	29.5	17.2	24.6	-30.1	70.3°	62.2°	.72	-28
2.3	43.6	17.8	24.3	-26.8	66.5°	59.6°	.80	-20
2.1	78.6	Just set.	24.3	∞	33°	58°	1.59	+59

Water value of viscosimeter = 10.2 seconds.

Time taken to apply each dose = 30 minutes.

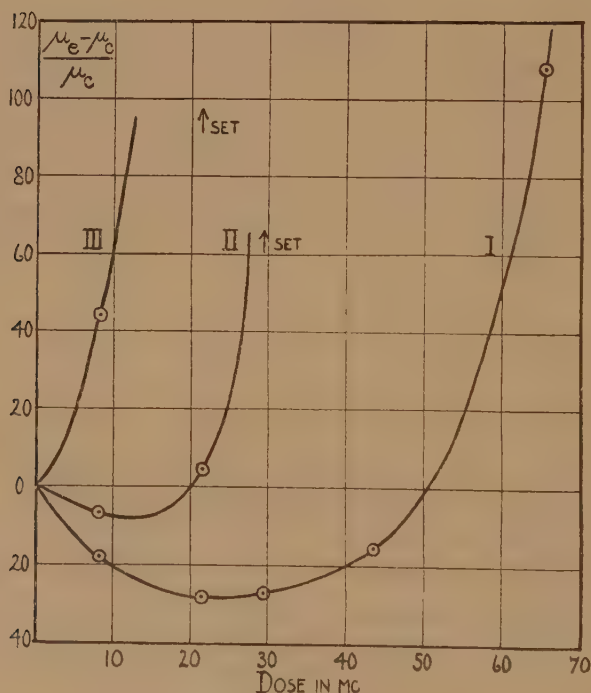
* Time taken to apply this dose = 45 minutes.

D. Gelling after the isoelectric point has been reached. (Fig. 7.)

Although it has not been definitely proved, it is reasonable and will be assumed that the position of minimum viscosity of the sol corresponds to the stage at which all the particles are discharged; that is, when the sol is at the isoelectric

point. The spontaneous setting which takes place after this point has been reached is not nearly so rapid as might be expected. Observations were made on a sol one-third the concentration of the standard stock sol. The percentage change in viscosity was plotted against the X-ray dose (curve I. fig. 7). The samples with which this curve was obtained were kept and measured again 21 hours and 92.5 hours after exposure (curves II. and III.). It is seen

Fig. 7.



that a sample which had suffered the maximum decrease in viscosity had only exceeded its original value by 4 per cent. after 21 hours. The sample with a dose of 29.5 mc., which was a little in excess of the completely discharging dose, had just set after 21 hours. It is quite safe to say that in the case of these sols of low concentration, the spontaneous setting which ensues after the minimum viscosity point has been reached takes at least several hours for completion. On the other hand, if irradiation is continued sufficiently beyond the isoelectric point, the sol sets immediately to a

clear stiff gel. The rays must be regarded therefore as accelerating the gelling process.

Data for the curves of fig. 7 are given in Table VI.

TABLE VI.

Distance of liquid surface from focal spot (clear), (cm.)	Dose (mc.).	μ exposed (seconds).	μ control (seconds).	$\frac{\mu_{\text{ex.}} - \mu_{\text{con.}}}{\mu_{\text{con.}}} \%$	Percentage change after 21 hrs.	Percentage change after 92.5 hrs.
5.30	8.24	16.33	19.95	- 18.3	-6.73	+43.8
3.30	21.26	14.37	19.85	- 27.4	+4.44	Just set.
2.80	29.50	14.91	19.98	- 25.4		
2.30	43.62	16.80	19.96	- 15.8		
1.88	65.20	41.75	19.95	+108.5		

Time taken to apply each dose = 44 minutes.

Water value of the viscosimeter = 10.2 seconds.

DISCUSSION.

It was pointed out in the previous paper that the effect of the radiation on the solution is to liberate a number of fast β -particles, each of which produces several hundreds of pairs of ions. On account of the intense electric field surrounding the particles, the ions produced in the electrical double layer will be drawn out of the field before any appreciable recombination has taken place. If the number of β -particles lost by a colloidal micelle is less than the number of ions captured, its charge will be neutralized. Calculation shows that this condition is satisfied. The particles will therefore be discharged by the rays with a consequent decrease in the viscosity of the sol. In the case of a hydrophobic sol, coagulation and precipitation begin directly the isoelectric point is reached. The stability of hydrophilic sols depends also on a second factor, the hydration. The particles of such a solution must be regarded as being surrounded by a ring of attached water molecules. When their charges are neutralized, this hydration persists and prevents them aggregating and precipitating. Instead, they cling together, producing an increase in viscosity, eventually forming a rigid framework or lattice when the solution sets to a gel.

The spontaneous gelling which sets in directly the isoelectric point is reached for any number of particles will, in more concentrated sols, mask the initial decrease in viscosity. This is happening in the curves of fig. 1. In a less concentrated sol, however, the time taken for a discharged particle to find a partner will be very much longer, and if the exposure is not too prolonged we may expect to study the initial viscosity decrease before coagulation has set in to any appreciable extent. Such a study is made in Section B.

The ageing of the sols is due to a gradual diminution of the charges on the particles with consequent slow coagulation.

Since the size of a colloidal micelle must be taken to include the surrounding ring of hydrating water molecules, the decrease in size up to the isoelectric point may be due to a decrease in hydration. It seems probable that the hydration will depend upon the charge on the particles, and that the smaller their charge the smaller are the forces binding the water molecules.

Discussing the coagulation of a ceric hydroxide sol by radium radiation, Freundlich* states "that only the discharge and the decrease in viscosity appear to be caused by the radium radiation, for the rise in viscosity also occurs when the radium preparation is removed from the sol at the moment when the viscosity is at a minimum." In this research X-ray doses sufficiently in excess of that required to produce complete discharge will coagulate the sol immediately, and can be regarded as accelerating the gelling process, which in the case of the sol investigated in Section D would have taken several hours for completion.

SUMMARY.

(1) A quantitative study is made of the viscosity changes produced in ceric hydroxide hydrosol by X-rays.

(2) *a.* In sols of low concentration and with increasing X-ray doses the viscosity decreases to a minimum, then increases rapidly and the sol sets to a rigid gel.

b. In more concentrated sols the spontaneous increase in viscosity which takes place when the particles are discharged masks the initial decrease.

c. The sols become more sensitive to X-rays with age, and the doses required to produce the maximum decrease in viscosity and to set the sol to a gel

* 'Colloid and Capillary Chemistry,' p. 485.

become very much smaller, indicating that the charge upon the particles is decreasing.

- (3) *a.* When the position of minimum viscosity is reached the sol sets spontaneously to a rigid gel within the course of a few hours.
b. An X-ray dose sufficiently in excess of that required to produce the maximum decrease will set the sol to a gel immediately.

(4) In a particular sol studied the particles decreased in size up to the position of minimum viscosity. The percentage decrease in size was almost equal to that in viscosity. Beyond the minimum point the particles increased in size, reaching a maximum at the setting point of 1.6 times the normal value.

In conclusion, I should like to thank Professor Crowther for his particular interest, kind help, and advice. He has intimated his intention, in a future paper, to review and comment upon the researches carried out in this laboratory during the past two years on the colloidal state of matter. I should also like to express my indebtedness to the Board of Scientific and Industrial Research for a grant which has made this work possible.

Department of Physics,
University of Reading,
June 8th, 1928.

XLII. On the Thermal Measurement of X-ray Energy. By J. A. CROWTHER, M.A., Sc.D., F.Inst.P., Professor of Physics in the University of Reading, and W. N. BOND, M.A., D.Sc., F.Inst.P., Lecturer in Physics.*

Introduction.

THE experiments described in this paper were commenced early in 1926 to determine the relation between the ionization produced by a beam of X-rays and the energy of the beam. The matter is of importance both from a theoretical and a practical aspect. In the first place, early experiments, as for example those of Rutherford and McClung, indicated that the work spent per ion during

* Communicated by the Authors.

ionization by X-rays was considerably greater than the ionizing potential of the gas ionized, and it is desirable that this result should be tested further. In the second place, it is generally agreed that the most suitable method of measuring quantities of X-rays is by the ionization they produce in some suitable form of ionization chamber, and it is clearly desirable that experiments should be made to determine exactly what it is that an ionization chamber measures. At the time when we commenced our work there seemed to be no adequate data on this point, and it was hoped that such data might be supplied by the experiments we had in mind.

Neglecting secondary effects which may be produced by the presence of the electrodes used for measuring the ionization current, the number of electrons produced per unit volume of air by the passage of a beam of X-rays can depend only on two factors, the energy conveyed by the beam, and the wave-length of the radiation, and can be written in the form $I = \phi(E, \lambda)$. If the values of E and I can be determined for a sufficient number of values of λ , the nature of the function can be determined. The ionization, I , can be determined in some suitable ionization chamber, and the energy E by absorbing the radiation completely in a calorimeter and measuring the energy in the form of heat. This is what we set out to do.

The necessity for such measurements seems to have become apparent to other experimenters at about the same time, and during the progress of our experiments a number of such determinations have been published, amongst others by Kriegesmann*, Kircher and Schmitz†, Kulenkampff‡, and Rump§. It appeared at first sight that further work on our part might be superfluous. Unfortunately, however, there was such strong disagreement between the values published by the different authors that further investigation became imperative. Thus Kriegesmann finds that the work spent in producing a pair of ions varies from 87.8 volts for X-rays of mean wave-length 0.397 Å.U. to 132 volts for a wave-length of 0.166, and states that the "volts" required to produce an ion-pair increases as the wave-length diminishes. Kircher and Schmitz, on the other hand, give a value of 21 volts per ion-pair, and find that it is independent of the wave-length. Kulenkampff, in a very long and elaborate

* Kriegesmann, *Zeit. für Phys.* xxxii. p. 542 (1925).

† Kircher & Schmitz, *Zeit. für Phys.* xxxvi. p. 481 (1926).

‡ Kulenkampff, *Ann. der Phys.* lxxix. p. 97 (1926).

§ Rump, *Zeit. für Phys.* xliii. p. 254 (1927), and xliv. p. 396 (1927).

paper, agrees that the energy spent is independent of the wave-length, but gives its value as 35 ± 5 volts per pair of ions. Finally, Rump gives values for the same quantity ranging from 300 volts for long wave-length radiation down to about 40 volts for filtered radiation from a hard tube. It was clear, therefore, that in spite of much recent work, the constant required was still in very considerable doubt. It was also clear that its determination was full of pitfalls, and that great care would be necessary to avoid both errors of measurement, and errors in evaluation of the constant from the measurements taken.

General Plan of the Experiment.

The radiation was produced by a Shearer tube working on a two-kilowatt transformer, and having a molybdenum anticathode. Two windows in the tube, closed with aluminium foil 1/20 mm. thick, allowed two narrow pencils of rays, one vertical, the other horizontal, to leave the tube. The horizontal beam passed through a small ionization chamber A, having parallel plate electrodes of aluminium. This chamber was used for comparison purposes only, as a means of eliminating the effect of fluctuations in the output; the actual measurements used in calculation were all made on the vertical beam. The tube was controlled by adjusting the supply of air to it by means of a micrometer air-leak. As the tube is self-rectifying its condition cannot be determined with any accuracy by means of a spark-gap, since the spark-gap measures only the peak potential in the circuit, which, in the case of a self-rectifying tube, occurs in the half wave which does not pass through the tube. The peak potential, when the tube is taking a current, will clearly be less, and may be considerably less than this. To overcome this difficulty a milliammeter with an open scale was inserted in the tube circuit, and an A.C. voltmeter was connected across the primary terminals of the transformer. It was found, experimentally, that a given pair of readings on these instruments corresponded to a definite state of the tube. If, for example, the voltmeter was set, by adjusting the primary resistance, to read 155 volts, and the milliammeter, by adjusting the leak, to read 3 milliamperes, the output from the tube was of definite quality and intensity, which was found to be reproducible at any time to an accuracy of at least 1 per cent. This method of regulating the tube is much more convenient than the use of a spark-gap, and seems to be at least as accurate.

The anticathode end of the tube was efficiently water-cooled. It was, however, of the utmost importance to prevent any thermal radiation from the tube from reaching the calorimeter in which the X-ray energy was measured. A "water-sheet" was therefore introduced between the tube and the calorimeter. This consisted of two parallel sheets of stout brass with a space about 1 mm. thick between them, through which a constant stream of water could be passed. A circular hole, 1.007 cm. in diameter, was pierced through the double sheet, the holes being covered with thin celluloid sheets to make the system watertight. This hole came immediately below the window of the tube, and served as the stop limiting the vertical beam passing into the calorimeter. Thus all the energy passing through the "water-sheet" passed directly into the calorimeter. Since it is convenient that the horizontal and the vertical beams should be of the same composition, sufficient thickness of cellophane was introduced into the horizontal beam to equalize the absorption of radiation in the vertical beam due to the water-sheet. The efficiency of the water screen is discussed in a later section.

After penetrating the water screen the vertical beam passed either into the calorimeter, which is described later, or into the ionization chamber which was used as a standard for the experiment. This chamber was furnished with a shutter, actuated by a carefully graduated micrometer screw, which limited the beam entering the chamber. The collecting electrode of this chamber could be connected, when desired, to the same electroscope as that attached to the comparison chamber A. A standard mica condenser could also be connected to the electroscope when necessary. The details of the ionization measurements will be discussed more fully in a later section.

The course of the experiments was as follows. The calorimeter was inserted in the path of the rays. The standard ionization chamber was cut out of the electroscope system, leaving the comparison chamber A attached to the electroscope and to the standard condenser. The tube was then excited, and kept working in its standard condition until the deflexion of the electroscope indicated a rise in potential of approximately one volt. The actual voltage was then measured by means of a potential divider in the usual way. The total charge which the X-rays had allowed to pass across the comparison chamber during the run could thus be measured. The condenser used was a subdivided microfarad, and the charge conveyed across the ionization chamber

in a single run was usually of the order of a microcoulomb. As evidence of the certainty with which the tube condition could be reproduced, it may be mentioned that the time taken to produce a charge of one microcoulomb on the condenser for a given setting of the tube did not vary by more than a few seconds in about eight minutes, over a period of some months.

In this way determinations were made of the heat produced in the calorimeter in relation to the charge conveyed across the comparison chamber. The calorimeter was now removed and the rays allowed to fall on the shutter of the standard chamber, which was now connected to the electro-scope system. The standard chamber was charged to a potential of opposite sign to that of the comparison chamber, and the area of the shutter was adjusted until a balance was obtained in the electroscope with the rays passing through both chambers. In order to increase the sensitivity, the condenser was removed from the system during balancing experiments. It was possible to balance the two currents to an accuracy of one part in a thousand. Balances on different occasions, however, were only consistent to about one per cent. These variations probably indicate the limits of certainty to which the tube conditions can be controlled.

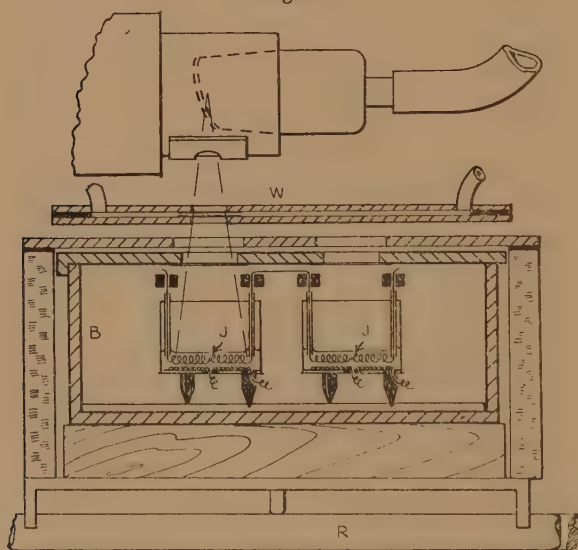
Assuming the whole area of cross-section of the vertical beam in the plane of the shutter to be known, the ionization which would have been produced if the whole of the X-ray energy which is absorbed in the calorimeter had passed through the standard chamber, is equal to the ionization as measured in the comparison chamber multiplied by the ratio of the cross-section of the whole beam to the aperture of the shutter. The results of these determinations are given in Tables III. and IV., and a more detailed account of the observations in the following section.

The Energy Measurements.

The accuracy of the energy measurements depends on our being able to absorb the whole of the incident X-ray energy, and to transform it into heat at the proper place. Owing to the phenomena of scattered, fluorescent, and corpuscular radiation, it is impossible to find a surface which will do this. The only reliable method is to pass the radiation into a box, the aperture of which subtends a sufficiently small angle at the surface on which the radiation actually falls. From the point of view of ease of measurement a thermocouple made of thin foil presents

many advantages. A suitably designed thermocouple will show a rise of one or two degrees when placed in a powerful beam of X-rays. It seemed, however, to be practically impossible to determine with any certainty what fraction of the X-ray energy would be lost by secondary radiation from the surface, using, as we were, heterogeneous beams. The fraction so lost would depend on the character of the radiation used, and from our estimates might conceivably be as high as 10 per cent. The calibration of such a thermocouple also presented difficulties. We decided, therefore, in favour of a calorimeter, using oil as the absorbing medium.

Fig. 1.



X-ray tube, "water-sheet," and calorimetric apparatus.

Calculation showed that, with the dimensions employed, the proportion of the energy lost was of the order of 1 per cent. Its exact determination was thus not of any great importance.

Actually, a pair of similar calorimeters was employed (fig. 1). Each calorimeter consisted of a vertical cylinder of thin plated copper, 2.8 cm. diameter and 2 cm. high, closed at the base by a plated copper sheet 1 mm. thick. The calorimeters, supported on short ebonite legs, stood side by side in a brass box B, 3 mm. thick, the top and one end of which were movable. The top of this box was pierced

by a pair of holes, each vertically over one calorimeter, the holes being covered with thin tissue-paper. The whole of this box could slide aside on rails R, so that the X-ray beam was no longer intercepted, but passed to a standard ionization chamber lower down.

The difference in temperature of the two calorimeters was estimated by a pair of thermo-junctions JJ, copper-eureka-copper (0.27 mm. diameter). Each calorimeter contained about $2\frac{1}{2}$ c.c. of light oil (such as is used in oil-immersed transformers), in which was located one of the thermo-junctions. The wire for a short distance on either side of the junction was wound into a horizontal helix, which, being in oil, should make the temperature of the junction at the centre fairly representative of that of the calorimeter. The eureka wire passed upwards out of one calorimeter through a glass tube, thence over an ebonite support and down through a second glass tube into the other calorimeter. The copper wires, similarly insulated, passed, without any joins, side by side to the galvanometer terminals. To avoid any possibility of the X-ray apparatus disturbing the galvanometer, the latter was situated in an adjoining room.

For purposes of calibration, a single-layer pancake coil of covered eureka wire, 0.27 mm. diameter, was fastened with shellac on the inside of the base of each calorimeter. The ends of these wires passed through ebonite in the base of the calorimeters, and at a short distance outside were joined to thin copper wires, which passed through ebonite bushes in the side of the brass box B, and there joined stout copper wires through which a small measured current could be supplied.

To screen the brass box, containing the calorimeters, from fluctuating supplies of heat, its sides were covered with asbestos board and cotton-wool, and its top with a cardboard sheet. (It rested below on a wood block.) Further to screen its top, and especially to prevent heat radiation from the X-ray tube from passing through the tissue-paper covered hole into the calorimeter, a "water-sheet" screen W was placed above. This consisted of two plates of brass (2 mm. thick), separated by a rubber edging, between which water was passed. Holes drilled in the brass sheets were covered with thin celluloid, so that a window was formed for the passage of the X-rays. Unlike the metal box B, the "water-sheet" was not movable, and its window formed a permanent stop, limiting the width of the X-ray beam. Any screens used to filter the rays were placed between the X-ray tube and this "water-sheet."

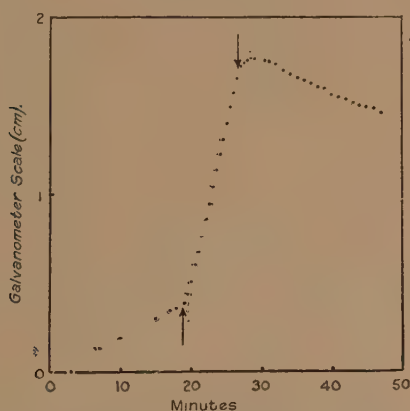
The copper wires from the thermo-junctions JJ were connected directly to a galvanometer of about 115 ohms resistance, giving about 23 mm. scale deflexion per micro-volt. As a result, a deflexion of $\frac{1}{10}$ mm. corresponded to about 10^{-4} °C. difference in temperature between the two calorimeters. In any experiment, the heating due to X-rays or to the current through the pancake coil was continued for about 7 minutes, and resulted in about $1\frac{1}{2}$ cm. galvanometer deflexion. Owing to the lag of the galvanometer and to the time required for heat diffusion in the calorimeter, the galvanometer did not attain its final rate of motion till about $1\frac{1}{2}$ minutes after the X-rays were started, or $2\frac{1}{2}$ minutes after the heating current through the pancake coil was started. To avoid the difficulty thus introduced, and to minimize any effects due to any slight fluctuation in the running of the X-ray tube, the total galvanometer movement, corrected for cooling, was deduced in each case. (At the same time, the total charge passed across the comparison ionization chamber was measured.)

When no heat was being supplied, the difference in temperature between the calorimeters decreased to half its value in about 8 minutes. The rate of cooling was, however, affected by slow heat waves, chiefly due to the X-ray tube and pumps. Therefore all subsidiary apparatus was put in action about an hour before any experiment, and the galvanometer reading was noted about every minute from considerably before till well after the experiment. (A typical set of results is shown in fig. 2.) The rates of galvanometer movement before and after the test were then used to deduce the total galvanometer reading corrected for cooling. The uncertainty in the value of any one cooling correction (the correction amounted on the average to about 20 per cent.) was minimized, and shown not to be large, by arranging to have the initial difference in temperature between the calorimeters varying in value and even in sign throughout a set of experiments.

For the heat calibration the resistance of the pancake coil (in the calorimeter in which X-rays were absorbed) was measured at the commencement and end of the experiments. The amount of the wire that was effective in producing heating of the calorimeter was able to be estimated to at least an accuracy of $\frac{1}{2}$ per cent. (see Table I.). The heating current was supplied by a 2-volt secondary cell, with about 230 ohms resistance in series. The current was measured by connecting a standard cell and table galvanometer across a

known part of this resistance; checks were obtained by changing the standard cell, changing the resistance box used, and by reversing the connexions of 2-volt and standard cells. The heat was supplied at about the same rate as in the X-ray experiments, and for about an equal time. A cooling correction was applied as in the main experiments, the pumps etc. being run during some tests and not during others. The corrected galvanometer deflexion for a joule of energy supplied to the calorimeter was thus estimated at various times during the course of the experiments, enabling the energy supplied during any X-ray absorption experiment to be deduced.

Fig. 2.



Thermal measurement of energy supplied by X-ray beam.
(Duration of X-ray heating indicated by arrows.)

The result of these experiments was:—

TABLE I.

Resistance of Calibrating Pancake Coil.

Eureka wire in calorimeter	9.46 ohms.
„ „ „ ebonite.....	0.08 „
„ „ outside calorimeter	0.31 „

Assumed effective resistance producing heating of calorimeter,
 $9.46 + 0.08/2 = 9.50$ ohms.

TABLE II.

Heat Calibration Experiments.

Heating current 0.00848 amp. (*i.e.* drop in potential across 120 ohms arranged to equal e. m. f. of standard cell, 1.018 volts).

Rate of energy supply to calorimeter, $9.50(0.00848)^2 = 0.000684$ watts.

Duration (min.).	Galvanometer deflexion (cm.) corrected for cooling.	Corrected galvanometer deflexion (cm.) per joule supplied to calorimeter.
5	1.66	8.08
7.08.....	2.29	7.88
7	2.20	7.65
8	2.68 ₅	8.17
7	2.28	7.62
6	1.92 ₅	7.81
5	1.68	8.18
7	2.37 ₅	8.26
Mean.....		7.99 ± 0.06

TABLE III.

Thermal Measurement of Energy supplied by X-ray Beam.

Series.	Galvanometer deflexion (cm.) corrected for cooling.	Microcoulombs passed across comparison ionization chamber.	Galvanometer (cm.) Microcoulombs comparison.	Joules supplied by beam Microcoulombs comparison. $\left(\frac{E}{I}\right)$
I.	$\begin{Bmatrix} 1.53 \\ 1.62 \\ 1.43 \\ 1.50 \end{Bmatrix}$	$\begin{Bmatrix} 0.542 \\ 0.545 \\ 0.567 \\ 0.545 \end{Bmatrix}$	$\begin{Bmatrix} 2.82 \\ 2.97 \\ 2.52 \\ 2.75 \end{Bmatrix}$	0.346 ± 0.009 (0.341)*
II.	$\begin{Bmatrix} 2.15 \\ 2.07 \\ 2.00 \\ 2.01 \end{Bmatrix}$	$\begin{Bmatrix} 1.045 \\ 1.045 \\ 1.03 \\ 1.03 \end{Bmatrix}$	$\begin{Bmatrix} 2.05_5 \\ 1.98 \\ 1.94 \\ 1.95 \end{Bmatrix}$	0.248 ± 0.003 (0.244)*
III.	$\begin{Bmatrix} 1.50 \\ 1.37 \\ 1.37 \\ 1.25 \end{Bmatrix}$	$\begin{Bmatrix} 1.10 \\ 1.105 \\ 1.075 \\ 1.035 \end{Bmatrix}$	$\begin{Bmatrix} 1.36_5 \\ 1.24 \\ 1.27_5 \\ 1.21 \end{Bmatrix}$	0.159 ± 0.003 (0.151)*

* The numbers in brackets are after applying a $1\frac{1}{2}$ -per-cent. correction for heat radiation, described in the next paragraph.

The above experiments seemed largely to have eliminated any error due to slow heat waves affecting the calorimeters unequally. It remains to test whether heat radiation in any appreciable amount was passing through the celluloid and flowing water that formed the window. The temperature attained by a screen of aluminium foil ($\frac{1}{10}$ mm. thick) that had been placed above the "water-sheet" to filter the X-ray beam was therefore measured. After copper-plating part of the lower face of the foil near the centre, a thermo-junction was soldered on. The running of the X-ray tube was found to cause the lower face of the foil to rise in temperature between 1° C. and $2\frac{1}{2}^{\circ}$ C., according to how good a thermal contact there was between the aluminium and the "water-sheet." That the measurement was not affected appreciably by heat conduction along the thermo-junction wires was shown by obtaining an almost identical result using much finer wires ($\frac{1}{15}$ mm. diam.). The aluminium foil was then heated electrically by a small coil placed above, and the heat reaching the calorimeter for a known temperature of the aluminium foil was measured (the X-ray tube not being run). When the foil was 19° C. above the temperature of the room, the amount of heat reaching the calorimeter was quite small compared with that received in the X-ray experiments. It was finally deduced that the heat radiation received from the foil during an X-ray absorption experiment amounted to rather less than 2 per cent. of the total heat measured.

Measurement of the Number of Ions produced.

As the experiments progressed, it became more and more clear that the real difficulties in the experiment would be concerned with the measurement of the ionization and not with the measurement of energy. The difficulty arises from the fact that the radiation from the anticathode of an X-ray tube is a mixed beam containing components of very different wave-length and absorbability. The beams used in our experiments, for example, contained components with a coefficient of absorption in cellophane ranging from more than 2.1 to something less than 0.4. Let us assume, as seems probable from the results of these experiments, that the number of ions produced by a beam of strictly homogeneous radiation is proportional to the energy absorbed from the beam in the ionization chamber. Since the coefficient of absorption is proportional to the cube of the wave-length, the ionization produced by the long-wave components in a mixed beam will be many times greater than

that due to the shorter wave-lengths, for equal intensities in the beam. Suppose, now, that to measure the absorbability of the radiation we insert a thin sheet of absorbing material in front of the ionization chamber. This will produce a marked absorption of the longer wave-length radiation, and, therefore, a large decrease in the measured ionization. The more penetrating radiation will have suffered little absorption in the sheet; but as its ionizing power is small, the presence of this penetrating radiation in the beam will not compensate for the loss of the softer radiation. In other words, the ionization method will overestimate the amount of energy absorbed from the beam. Consequently, any estimates of the fraction of the energy absorbed in an ionization chamber, made from coefficients of absorption so determined, will be seriously in error.

We were able to demonstrate this effect quite conclusively from our readings. It was found that the introduction of 0.2 mm. of aluminium into the beam from our tube reduced the measured ionization by 45 per cent. in a particular case. The energy of the beam as measured calorimetrically was, however, only reduced by 25 per cent. The discrepancy under actual experimental conditions may thus be very large. The point may seem to be so elementary as to be hardly worth making. It is, however, easily overlooked, and, in fact, several of the calculations in the papers on X-ray energy already mentioned are made on this basis, or on the basis of a mean wave-length calculated from such absorption measurements. This probably accounts for at least some of the differences in their results. Where the beam is a mixed one the attempt to translate coefficients of absorption into mean wave-lengths can serve only as a rough indication of the quality of the rays. Any calculations based on this method are liable to serious error.

As the fraction of the energy absorbed in the ionization chamber cannot be deduced from absorption experiments, we are reduced to determining the total number of ions formed by the complete absorption of the radiation. As a column of air 1 metre long would only absorb some 25 per cent. at most of the radiation employed, this determination cannot be made directly. We can, however, arrive at it indirectly as follows. If I is the intensity of the X-radiation, the ionization in a chamber containing air of mass per unit area dm will be $I \cdot dm$. The total ionization produced

by the complete absorption of the beam is thus $\int_0^{\infty} I \cdot dm$.

If I_0 is the initial intensity of the radiation, the ionization in

the ionization chamber, as measured in the energy experiments, is $I_0 \cdot \Delta m$, where Δm is the mass per unit area of the air in the chamber and is equal to $l\rho$, where ρ is the density of air, and l the length of the path of the rays through the chamber. The value of I , the intensity of the radiation, can be found in arbitrary units by using a small ionization chamber and measuring the ionization with gradually increasing thicknesses of the absorbing material between the chamber and the source of radiation. The area, α , of the curve obtained by plotting I against m will be the required integral, and $\frac{1}{I_0} \int_0^\infty I \cdot dm$ the required correcting factor.

In practice it is not possible to use air as the absorbing material, and the experiments were actually made using cellophane sheets. Cellophane is a convenient form of cellulose, and from its composition we might expect that its properties as regards X-ray absorption would not differ markedly from those of air. To obtain the true area of the curve, however, the ionization must be plotted not against the mass of cellophane employed, but against the mass of air which would produce the same absorption. This involves a knowledge of the relative absorbing powers of air and cellophane.

According to the makers, cellophane is pure cellulose, and the ratio of the mass absorption of cellophane to that of air should thus be calculable from the atomic coefficients of absorption. This calculation gave the value 0.84. Owing to the marked influence of traces of impurity of high atomic number on the absorption (the argon in the air accounts for 12 per cent. of the total absorption), it was deemed wiser to measure the required ratio directly. The rays were accordingly passed through a wide tube one metre in length, with thin cellophane windows, the tube being evacuated to any desired pressure. The ionization in a suitable chamber placed at the far end of the tube could be balanced against that in the standard chamber, by means of the adjustable shutter. A balance was first obtained with the tube full of air at atmospheric pressure. Five sheets of cellophane, each of mass per unit area 0.0243 gm./cm.², were interposed in the beam, and the chamber evacuated until the balance was restored. The reduction in pressure required was found to be 67.3, 67.3, and 67.5 cm. for the three classes of radiation used in our experiments, at a temperature of 19°C., giving a ratio of air to cellophane of 0.880, independent of the quality of the radiation. The experimental value was

employed in the calculations. The difference between the calculated and the experimental values is no doubt due to the presence of metallic impurities in the cellophane. This suggestion was confirmed by an "ash" test on the substance, which was found to yield about 0.4 per cent. ash, containing principally sodium and calcium as its metallic constituents. Each absorption curve was continued until the ionization had been reduced to 3 per cent. of its initial value, so that the true area of the curve could be determined without uncertainty as to the nature of the end radiation. The values so obtained for the factor $\frac{1}{I_0} \int_0^\infty I \cdot dm$ are given in the fourth column of Table IV.

A further correction is necessary to allow for the radiation scattered out of the direct beam. The ionization due to the scattered radiation is clearly not included in the ionization measurements. If E is the energy of the primary beam, μ the mass coefficient of absorption, and σ the mass coefficient of scattering, then the total energy S scattered out of a narrow pencil of rays is given by

$$S = \int_0^\infty \sigma E e^{-\mu m} dm = \frac{\sigma}{\mu} \cdot E.$$

Unfortunately, we cannot apply this relationship directly to our measurements, for, as we have already pointed out, the mean wave-length, however calculated, is only a very rough test of the quality of a heterogeneous beam, and the coefficients of absorption, as deduced from an absorption curve, are liable to be in very serious error.

The only adequate solution of the difficulty is to analyse the radiation spectroscopically. When the distribution of energy among the various wave-lengths is known, the relation already given can be applied separately to each constituent of the heterogeneous beam, and the value of S for the whole beam can thus be determined. Fortunately, Mr. L. G. Treloar has been engaged for some little time in this laboratory in analysing the radiation from a Shearer tube under different conditions, and we have been able to select from his results, which will shortly be published, distribution curves corresponding to the conditions of working in our experiments. In this way values were obtained for S/E for the three types of radiation used in our experiments. The total measured ionization is due to the absorption of $E - S$ units of energy, instead of the E units measured in the calorimeter, since S units have been scattered from the beam and produce their ionization

elsewhere. To obtain the true value of the energy spent per ion we must therefore multiply our measured energy by $\frac{E-S}{E}$. The calculated values of this ratio are given in column 5 of Table IV.

Although the method seems sound, the calculation of the scattering correction is probably the least satisfactory part of the work. The values for the scattering coefficient σ and the values of μ the mass absorption coefficients for different wave-lengths have been calculated from tables of values collected by Compton. In spite of the large amount of work which has been done on the subject, the values given by different authorities are not in very close agreement, and we have not felt justified in giving this correction to more than two significant figures. An error of 10 per cent. in estimating S/E only introduces an average error of about 3 per cent. into the correcting factor, and we consider that the latter should be correct to this amount. It may be mentioned that the coefficients used in calculating the scattering correction are the only data employed in our calculations which have not been directly measured in our experiments.

Measurements and Results.

It will be appreciated from the previous sections that the determination of the energy spent per ion for radiation of given quality involved a very considerable amount of experimental work. On the other hand, owing to the possibility of deterioration in the tube with prolonged usage, it was desirable that the experiments should not be unduly prolonged. It was decided, therefore, to concentrate on three standard beams: (I.), with the tube running at the highest potential at which it was possible to secure steady working, about 55,000 volts, and filtering the radiation through 0.3 mm. of aluminium; (II.), with the tube as in (I.), but with a filter of only 0.1 mm. of aluminium; and (III.), with the tube running at the minimum potential which would give a beam of sufficient intensity to measure calorimetrically. This radiation was also filtered through 0.1 mm. of aluminium. The water screen was, of course, present in all experiments. These limits were fixed by the capacity of the apparatus, and the average quality of the radiation in the three beams did not differ very widely, though the difference was appreciable. The initial mass coefficients of absorption in cellophane were 1.0, 2.0, and 2.6 respectively, but as we have already pointed out, the coefficient

of absorption is not a reliable index of the average quality of the radiation. A better estimate may perhaps be obtained from the area of the absorption curve. For homogeneous

radiation the value of $\frac{1}{I_0} \int_0^\infty I \cdot dm$ is equal to $\frac{1}{\mu}$. If we

write $\frac{1}{\bar{\mu}} = \frac{1}{I_0} \int_0^\infty I \cdot dm$, we can perhaps regard $\bar{\mu}$ as a

kind of mean coefficient of absorption, and the corresponding wave-length as a mean wave-length. The values of μ in air deduced in this way are respectively 0.86, 1.12, and 1.48. The wave-lengths which would correspond to these absorption coefficients if the radiation were homogeneous are 0.60, 0.68, and 0.75 Å.U. The range is not a very wide one. It is hoped to extend it in the near future, when more powerful apparatus is available.

The calculation of the energy expended by the rays for the production of a pair of ions was made as follows. The calorimetric measurements recorded in Table III. give the energy in joules collected by the calorimeter during the passage of one microcoulomb across the comparison chamber. This corresponds to the passage of one microcoulomb across the standard chamber when the aperture of this chamber is adjusted for compensation. The shutter reading, a , for this balance is given in column 3 of Table IV. The area of the aperture is the shutter reading multiplied by the width, d , of the aperture. If the whole beam had passed through the ionization chamber, the ionization produced would be increased in the proportion A/ad , where A is the cross-section of the beam at the level of the shutter. This area was determined geometrically, the necessary readings being made with a cathetometer. The value obtained this way was 12.96 cm.² Measurements made by exposing a photographic plate to the beam gave a value of 13.1 cm.² The two methods are thus consistent to 1 per cent.

The ionization produced in a layer of air of unit mass per unit area is obtained by dividing by the length, l , of the path of the rays in the ionization chamber, multiplied by ρ , the density of the air. The total ionization which would have been produced by the complete absorption of the beam is

obtained by multiplying by $\frac{1}{I_0} \int_0^\infty I \cdot dm = T$, the values

of which are given in column 4 of Table IV. The ionization is thus obtained in microcoulombs. The fraction of the whole energy used in producing this ionization is

$\frac{E-S}{E}$. Hence, since 1 ionic charge is equal to 1.591×10^{-13} microcoulombs, we have finally

$$\text{joules per microcoulomb} = \left(\frac{E}{I}\right) \times \frac{d \cdot \rho}{A} \cdot \frac{1}{T} \cdot \frac{E-S}{E} = \frac{E_J}{Q_M},$$

$$\text{ergs per ion pair} = \frac{E_J}{Q_M} \times 1.591 \times 10^{-13} \times 10^7,$$

$$\text{or "volts" per ion pair} = \frac{E_J}{Q_M} \times 10^6.$$

The values of the various quantities are given in Table IV. In calculating the last column, a small additional correction has been applied for the absorption of the beam in the column of air between the calorimeter and the standard ionization chamber. This correction varies from 1.5 per cent. in set I. to 3.6 per cent. in set III.

TABLE IV.

Series.	Joules per m.c. (measured) (E/I).	Aperture of shutter (a) (cm.).	$\frac{1}{I_0} \int_0^\infty I \cdot dm$ =T.	Scattering correction (E-S)/E.	Energy per ion pair in "volts."
I.	0.341	1.128	1.168	0.71	44.2
II.	0.244	1.085	0.892	0.75	42.0
III.	0.157	1.292	0.675	0.75	43.3

A=area of beam at shutter=12.96 cm.²

d=width of shutter=0.665 cm.

l=length of path of rays in chamber=3.125 cm.

ρ=density of air at 18° C. and 760 mm. pressure=0.00120 gm./cm.

Discussion of Results.

The results of the experiments are collected in the last column of Table IV., and, on the whole, are in very satisfactory agreement. There is no evidence that the energy abstracted from a beam of X-rays for the production of one pair of ions varies with the quality of the radiation over the range of our experiments, and we are justified in combining the results of the three sets of experiments. The measurements of the constants for the apparatus are certainly correct to well within 1 per cent., and the same applies to the measurements from which columns 3 and 4 of Table IV.

were calculated, as these measurements were made by the balance method, which, for comparatively large ionization currents such as we had to deal with, is susceptible of very considerable accuracy. Assuming that the variations in the results are due mainly to the errors in the heating experiments (given in Table III.), we obtain for the energy spent per ion 44.2 ± 1.2 , 42.0 ± 0.5 , and 43.3 ± 0.8 volts. Taking the weighted mean of these observations we obtain as our final result 42.5 ± 0.4 volts per ion pair.

There are, however, two factors which might affect the mean value. The first is the scattering correction which has already been discussed in detail. The mass coefficient of scattering for air was taken as 0.164, and the coefficients of absorption for various wave-lengths were taken from the table of mean values given by Compton. Any errors in these coefficients would affect the three correcting factors to very much the same extent. Fortunately, the scattering correction is not a very large one, so that the accepted values used in the calculations would require to be in very considerable error to produce any appreciable error in our mean.

The remaining factor which has to be considered is the efficiency of the standard ionization chamber. It may be desirable, therefore, to describe it somewhat more minutely. The collecting electrode was an aluminium plate, 3 cm. square, furnished with an aluminium guard ring 9 cm. square. The charged electrode was an aluminium plate, also 9 cm. square, placed parallel to the first at a distance of 2 cm. The field across the centre of the electrodes was thus uniform to a high degree, and the mass of gas from which the electrons were collected could be determined with certainty.

The radiation passed centrally between the electrodes, the width of the beam being 0.8 cm. at the centre of the plates. The apparatus was so adjusted that any radiation which might be scattered from the water-cooled stop, which limited the beam, would not be able to reach the electrodes. It was found experimentally that the ionization current across the chamber became saturated with a potential of about 350 volts on the plate; a potential of about 500 volts was actually used during the experiments, giving a field of 250 volts per cm.

To obtain the full ionization produced by the rays, it is further necessary that the photo-electrons ejected by the radiation from the air shall be completely absorbed before reaching the electrodes. As it was somewhat difficult to obtain any reliable data on the range of the photo-electrons,

the matter was tested experimentally, the ionization current being measured, by the balance method, with different distances between the electrodes. It was found that the ionization current remained constant as the distance between the plates was increased from 1.9 cm. to 3.0 cm. At distances greater than 3 cm. the current began to diminish, owing to the impossibility of producing complete saturation with the potential available. We can assume, therefore, that there was no detectable loss of ions through photo-electrons reaching the electrodes before producing their full ionizing effect. Further experiments indicated that the ionization current was independent of the material lining the walls of the chamber. As far as our tests go, they indicate that the chamber was completely satisfactory.

It is interesting to compare the value obtained in these experiments with those obtained in other recent investigations. The very variable values obtained by Kriegesmann *, ranging from 282 to 87 volts per ion pair, are probably ascribable to the unsatisfactory method of computing the results. The very low value of 22 volts given by Kircher and Schmitz * is completely out of accord not only with our own results, but also with those of all other observers. We cannot suggest any explanation of this low value. Kulenkampff *, after a very elaborate and careful set of observations, suggests a value of 35 ± 5 volts per ion pair, and his work deserves consideration. The energy measurements were made by allowing the radiation to fall on a thin silver foil, the temperature of which was taken with a set of thermocouples. There is much to recommend this method from the experimental point of view. The reduction of the thermal capacity from the 2 or 3 grams required for a calorimeter, to perhaps $\frac{1}{10}$ gram or even less of the bare thermocouple, makes the temperature readings much easier. We abandoned it deliberately for two reasons: firstly, the impossibility of knowing what fraction of the incident energy might be re-radiated as scattered, fluorescent, and corpuscular radiation; and, secondly, the difficulty of calibrating such a system.

Both uncertainties seem to attach to Kulenkampff's work. Apparently no correction is applied for the re-radiated energy, though this might possibly amount to as much as 10 per cent. Two methods of calibrating the thermocouple system were tried, and differed by 10 per cent. The mean of these results was used in the calculations. If the higher,

* *Loc. cit.*

and apparently the more reliable, estimate had been taken, the final value would have been increased by about 5 per cent. These possibilities are probably covered by the very generous margin of ± 5 , which Kulenkampff allows to his mean value. The points which we have raised, however, indicate that the true value should lie somewhere near the upper limit of his range.

There remain finally the experiments of Rump *. Rump's values range, as we have already mentioned, from about 300 volts per ion for very soft rays, down to round about 42 volts per ion for heavily-filtered radiation from a hard tube. The large values given for the soft radiation are undoubtedly due to his unsatisfactory method of dealing with his observations, as we have already pointed out in an earlier section of the paper. It is only fair to Rump to state that he recognizes this in the concluding paragraphs of his paper; but as he had not taken the measurements necessary for a proper calculation, he has to be satisfied with suggesting that the lower values obtained with the filtered radiation are probably the more correct. The effect of filtration is to concentrate the radiation towards the short wave-length end of the spectrum, and thus to reduce its heterogeneity. His values for filtered radiation range from about 39 to 44 volts per ion pair, with a probable mean of about 42 †. They are thus in close agreement with our results, although they apply to a very different part of the spectrum.

Summing up the discussion, we may conclude that the energy abstracted from an X-ray beam for the formation of a pair of ions is not very far removed from 42 volts, and that there is no evidence that this value varies with the wave-length of the radiation, though further evidence on this point is desirable. Since the ionization produced by X-rays is ascribed to the action of the photo-electrons produced by it, it is interesting to note that Meitner found for the energy spent per ion by β -radiation a value of 45 volts.

The ionization potential of the nitrogen and oxygen molecules is about 17 volts. The energy necessary to produce ionized atoms of nitrogen and oxygen from the molecule is, according to Smyth ‡, respectively 28 and 23 volts. It is evident, therefore, that a very considerable portion of the energy of an X-ray beam is not spent in

* *Loc. cit.*

† He later (*loc. cit.*) reduces his estimate to 33 volts per ion pair.

‡ Smyth, Proc. Roy. Soc. civ. A, p. 121 (1923).

producing ions, but degraded in some other way. The most probable method seems to lie in the production of δ -radiation, the very low velocity electrons which are given off in considerable quantity from the surface of a solid on which a beam of X-rays falls. If we assume that the process of ionization commences with the projection from the molecule of a δ particle, the average energy of these particles would be $(42-17)$ volts, or 25 volts. Our knowledge of δ -radiation is very limited, but the velocities of the particles escaping from a solid surface are of this order of magnitude. Investigations on this point are now in progress in this laboratory, and may throw further light on the mechanism of X-ray ionization.

In conclusion we may consider, very briefly, the application of these results to the ionization method of measuring X-radiation. Assuming that the energy spent per ion is independent of the wave-length, the number of ions produced in an air ionization chamber is directly proportional to the energy absorbed in it, each pair of ions being accompanied by the absorption of 42.5 "volts" or 6.76×10^{-11} erg. The transference of 1 e.s.u. across the chamber thus indicates the absorption of 0.141 erg. Thus

$$I = 0.141 dE,$$

where I is the charge collected in e.s.u., and dE is the energy absorbed. If τ is the "true" mass absorption coefficient of the radiation, and dm the mass of air subjected to the rays in the chamber,

$$I = 0.141 E \cdot \tau \cdot dm,$$

or for 1 c.c. of air at 18° C. and normal pressure

$$I = 0.141 \times E \cdot \tau \times 0.00120 = 1.70 \times 10^{-4} E\tau.$$

It must, however, again be pointed out that this result can only be applied to homogeneous radiation, as measurements made in the usual way on the "coefficient of absorption" of a heterogeneous beam do not give even an approximately correct value for the energy absorption of the beam.

Summary.

(1) The energy of a beam of X-rays has been measured by converting it into heat in a calorimeter.

(2) The energy absorbed from the radiation for the formation of one pair of ions in air is 42.5 "volts."

(3) This value is constant over the range of wave-lengths employed in the experiments.

(4) The quantity of electricity, I , measured in electrostatic units across 1 c.c. of air at 18°C . and normal pressure is given by

$$I = 1.70 \cdot 10^{-4} E\tau,$$

where E is the total X-ray energy in ergs which has passed through the gas, and τ is the "true" mass coefficient of absorption. The relation cannot be applied to a heterogeneous radiation, owing to the impossibility of determining τ for such radiation.

In conclusion, the authors wish to express their obligation to the Government Grants Committee of the Royal Society for a grant made to one of them (J. A. C.) for the purchase of essential apparatus.

Department of Physics,
The University, Reading,
June 9th, 1928.

XLIII. *Selective Adsorption from Gaseous Mixtures by a Mercury Surface formed in the Mixture.* By M. L. OLIPHANT, 1851 Exhibition Research Student*.

Introduction.

THIS paper presents experimental evidence which indicates that an expanding mercury surface selectively adsorbs carbon dioxide from a mixture of carbon dioxide with an excess of hydrogen or argon. The measurements show that within the limits of the experimental error the carbon dioxide so adsorbed forms a monomolecular layer over the surface of the mercury.

When a mercury surface expands or is created, fresh atoms of mercury find their way from the interior of the liquid to the free surface. It is improbable that the atoms of mercury are absolutely symmetrical in the sense that the forces on neighbouring atoms are independent of their orientation, and it is unlikely that the fresh atoms of mercury which enter the surface are all oriented in the same way. A surface which is freshly formed *in vacuo* will speedily rearrange its constituent atoms in such a way that the energy in the surface is a minimum. This rearrangement will take place very rapidly, so that it is impossible to

* Communicated by Sir E. Rutherford, O.M., F.R.S.

measure the resulting rapid fall in surface-tension, after the formation of the surface, by any ordinary means. However, when a surface is expanded in contact with a gas, a mercury atom which comes into the surface with an active "end" outward will possibly remain in such a condition for some time, as it is able to form a "compound" with a gas molecule which may have a life of several minutes. Thus the rearrangement of the surface to form one of the lowest energy will be delayed by the adsorption of a gas layer, and it becomes possible to measure the decrease in surface-tension from a very high initial value to a lower final value which is approached asymptotically. The changes in the surface-tension which measure directly the decrease in the free energy of the surface are accompanied by concomitant changes in the other surface properties. Thus Popesco* has shown that five seconds after the formation of a large drop of mercury in contact with a gas the surface-tension is above 500 dynes/cm., and that this falls exponentially to a final value of about 400 dynes/cm., the time taken varying with the gas. He has also shown that the photo-electric effect obtained at the surface with a given source of light shows changes which follow the same general course. Perucca† has demonstrated that the contact potential of the surface against platinum shows changes of the same character. He has observed that the time taken to reach equilibrium is longer with carbon dioxide than with hydrogen, indicating that the former gas is the more rigidly held at the surface.

On the other hand, Harkins‡, using the "drop-weight method" for measuring surface-tension, does not observe any large difference between the surface-tension of a drop formed *in vacuo* and one formed in a gas. This would indicate either that the gas is not adsorbed at the surface so as to interfere with its orientation, or that the assumed abnormally high initial surface-tension due to the random orientation in the fresh surface does not actually exist. One of the methods for measuring the surface-tension must give the wrong result, and the following experiments have been carried out in order to test whether the adsorption of gas does take place at an expanding mercury surface. The problem of the surface-tension of mercury remains unsolved, but these results give definite evidence in favour of the "large-drop method" as opposed to the "drop-weight method" for measuring this quantity.

* Popesco, *Ann. d. Phys.* iii. p. 402 (1925).

† Perucca, *C. R.* clxxv. p. 519 (1922).

‡ Harkins, *J. A. C. S.* 1920.

Langmuir* has measured the adsorption of gas at plane surfaces of mica and glass carefully packed into a vessel and separated so as to avoid capillary spaces. In this way he obtained a large area in a moderate volume, and was able to measure the fall in pressure of the gas when admitted at low pressure into the vessel maintained at very low temperatures. It is obviously not possible to apply this method to mercury, for there is no conceivable method by which a large surface of perfectly pure mercury could be created in contact with a very small volume of gas. For this reason use has been made of a comparative method only, whereby the change in composition of a mixture of gases is measured. Owing to the fact that some gases are apparently held to the surface by greater forces than those holding others, a surface which is exposed to a mixture of gases should become covered with an almost complete layer of the more closely-held gas, that is the gas whose life on the surface is longest. Thus, if a stream of mercury drops be allowed to fall down a column of a mixture of two gases, the more easily adsorbed should be largely removed from the top of the column and given up where the drops collect in a pool at the bottom. If it were possible to eliminate the effect of diffusion back and of the stirring action of the falling drops, it should be possible to deduce, from a knowledge of the change in composition of the gas at the top, or the bottom, and the total surface of the falling drops, the amount of the one gas transferred per square centimetre of surface. This yields at once the adsorption in molecules per square cm.

Schofield† has developed an ingenious method by which the disturbing effects may be eliminated and the adsorption measured in the case of liquids (ion adsorption from solution); and this is the basis of the method by which the present problem has been attacked.

Method.

Consider a stream of mercury drops falling through a column of gas and collecting together at the bottom. As the drop forms at the top, its surface is continually expanding so that the surface in contact with the gas is always one freshly formed. Gas is adsorbed at such a surface very readily, and if the atmosphere is a mixture of gases, one will in general be adsorbed more readily than the others; for instance, as we shall see later, carbon dioxide is selectively

* Langmuir, *Phys. Rev.* viii. p. 149 (1916); *J. A. C. S.* xl. p. 1361 (1918).

† Schofield, *Phil. Mag.* ser. 7, i. p. 641 (1926).

adsorbed from a mixture of this gas with hydrogen or argon.

When the drop separates, it carries this carbon dioxide down with it and gives it up when it merges with the pool of metal below, for there the surface contracts to zero. The concentration of this gas at the bottom therefore increases, while that at the top decreases, but a limit is soon reached when this concentration gradient ceases to grow, owing to the mixing action of the falling drops. This effect has been largely eliminated by using Schofield's flow method, as has already been mentioned. A stream of the mixed gases, fed into the column at the middle, divides there into an upward and a downward stream of equal velocity, which flow out from the immediate vicinity of the points at which the drops form and where they coalesce. This stream is quite slow, but is sufficient to sweep away the carbon dioxide carried down by the drops as fast as it is given up below, while the upper stream is correspondingly impoverished. The effect of the mixing of the gas over the length of the column is thus very largely eliminated, for it is only at the very beginning and end of the path that these effects would be serious, and here the gas is swept away from these disturbing influences as fast as it accumulates. A great disadvantage is that the concentration change is thereby rendered very much smaller than when the gas is at rest, and it becomes necessary to use a very sensitive method for measuring it. An attempt to detect it by means of the difference in heat conductivities due to the difference in composition in the case of a mixture of carbon dioxide and hydrogen proved abortive, and this method was abandoned for an improvised Rayleigh gas refractometer with tubes two metres long. At a concentration of 2 per cent. carbon dioxide in hydrogen this proved capable of detecting a change of .001 per cent., and except at the very highest concentrations, proved entirely satisfactory. The change measured is the difference in concentration of carbon dioxide in the two limbs of the apparatus, that is twice the change in concentration of either stream alone.

If V be the volume of mercury falling as drops in one second and N the number, the surface exposed to the gas per second is

$$A = 4\pi N \left(\frac{3}{4} \frac{V}{\pi N} \right)^{\frac{2}{3}}.$$

Now each square centimetre of this surface will adsorb, say, n molecules, so that the total number transferred each

second will be nA . If the volume of gas traversing the apparatus at a temperature T and pressure P be v , the total number of molecules passing per second will be

$$S = v \times \frac{6.06 \times 10^{23}}{22.4 \times 10^3} \times \frac{273}{T} \times \frac{P}{760}.$$

The transferred molecules will constitute part of the stream traversing the lower limb, and a correspondingly smaller number of carbon-dioxide molecules will traverse the upper. In either case the concentration change will be very nearly given by $C = \frac{nA}{S} \times 100$, expressed as a percentage of the total volume passing. C is obtained from the interferometer, and knowing the other factors, n may be calculated. The measurements are carried out in practice in the following manner.

Experimental Details.

The apparatus was arranged as shown in fig. 1.

Mercury from the reservoir A, maintained at a constant level H, is delivered through a regulating tap T_1 to the stainless steel nozzle N fastened over the end of the glass tube with sealing-wax. This nozzle is perforated with twenty-five holes, each of which delivers about twenty drops per second. These drops fall down the tube F and collect in a pool at the bottom, whence the mercury flows out through the siphon S, finding its way through P_1 to the pump which returns it to the reservoir. The design of a pump which would circulate the mercury without contamination has proved the most tedious part of the investigation. An all-steel reciprocating pump proved unsuccessful, as it seized almost at once, owing to the impossibility of using any lubricant whatever. Abortive attempts at substituting a liquid (distilled water) piston for the steel were followed by a rotating design, which, after modification, worked very satisfactorily.

A drum D (fig. 2) of mild steel, lined throughout with sealing-wax after boiling in caustic soda and heating to a dull red, is mounted on the shaft of the motor M, and rotates at about 1400 revolutions per minute. The incoming stream of mercury is fed through the space between the inner and outer tubes of L, and falls through the hole H into the drum. The bent tube S scoops up mercury from the rotating shell of the metal which lines D, and delivers it through the axis of L to the reservoir. The compound tube L is clamped securely in a wooden block so that it passes

through the hole in the drum axially. This arrangement secures great rigidity and permits the construction of these parts of pyrex glass. The scooping action of S gives rise to

Fig. 1.

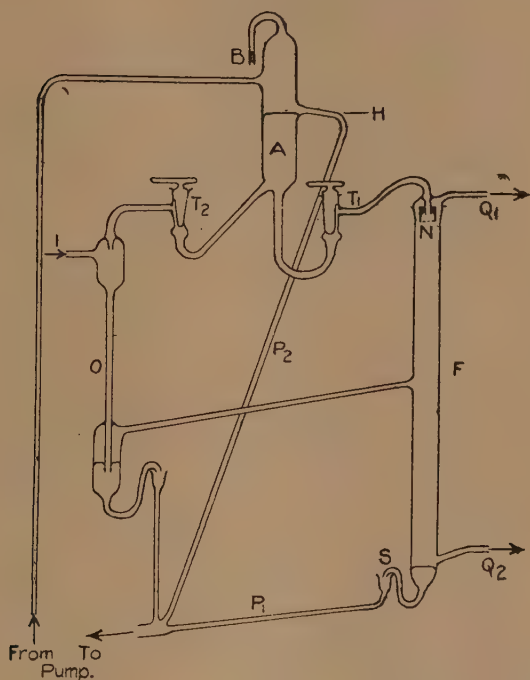
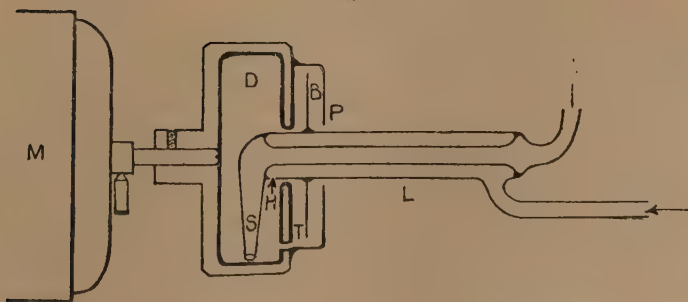


Fig. 2.



a spray of mercury drops in D, some of which escape through the clearance space between L and the drum. To avoid this a baffle B is stuck to the tube with sealing-wax and enclosed in a chamber P, a shallow glass dish, also fixed

with sealing-wax to the drum, and with a hole bored through the bottom. A small hole T is bored through the face of the drum at the periphery of this dish, and allows the mercury which collects in P to find its way back to the body of the pump. This circulating device runs smoothly and silently, and does not give rise to vibration of the bench to the extent that the reciprocating types did, while it possesses the great advantage of supplying a continuous stream of mercury whose rate of flow automatically adjusts itself to the rate at which mercury is supplied to the pump. In this way the level of the reservoir is maintained very constant, and the rate of dropping from the nozzle correspondingly so.

The mixture of gases which is to be used is fed at a constant rate into the centre of the fall tube F (fig. 1) by means of a Sprengel pump O with a fall of about 25 cm. The mercury for this pump is also supplied from the reservoir A through T₂, and after use is returned to the pump. The excess mercury supplied by the pump escapes down the overflow P₂.

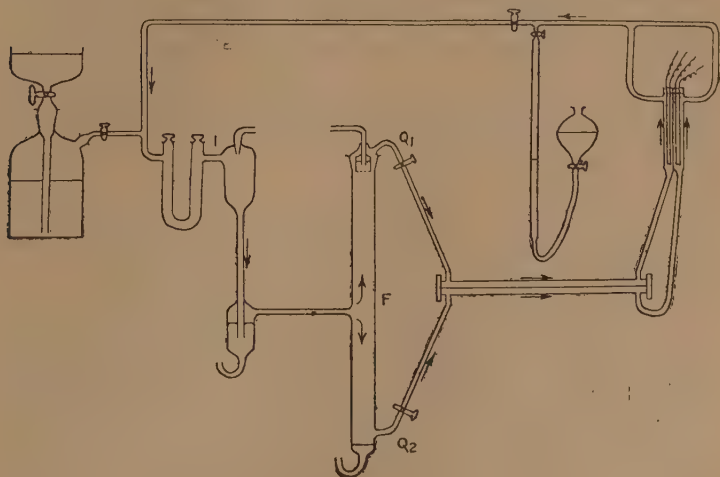
The stream of mixed gases divides at the centre, half passing upward and half down, thence through Q₁ and Q₂ to the two tubes of a Rayleigh interferometer. After traversing the interferometer the streams pass through two glass tubes down the axes of which fine platinum wires are sealed. These wires are heated by a current and balanced on a bridge, and they serve to maintain an equal rate of flow in each limb of the apparatus, any want of balance being rectified by adjusting the rate of flow. The difference in conductivity of the two streams, due to the slight difference in composition brought about by the adsorption, is not sufficient to affect the balance. The two streams then unite and are conducted back to the inlet I. A reservoir of the mixed gases is connected by a T-piece just before the stream reaches I and serves to maintain the pressure in the system at a constant value. A two-way tap connected at the same point allows the rate of flow to be observed at any instant by measuring the volume of gas collected in a burette in 10 seconds. The gas reservoir and the burette are filled with pure paraffin-oil in place of water in order to avoid loss of gas by solution. Just before entering at I the gas is thoroughly dried by passing over P₂O₅. A plan of the whole system showing the path of the gas through the apparatus is given in fig. 3.

The whole of the glass parts of the apparatus are of "pyrex," thoroughly cleaned with hot chromic acid and distilled water before assembling. The connexions and the

gas tubes are thick-walled pressure tubing which had been boiled in caustic soda and distilled water, and rubber-grease was smeared over the ends of all the glass tubes before pushing the rubber over. The mercury to be used is purified in the manner described by Burdon *, and is of similar quality to that used for other work on mercury surfaces in this laboratory. The apparatus was washed through with this mercury till that which escaped through S was good enough for distilled water to spread on it. In order to avoid effects due to temperature changes, the whole was assembled in an underground constant-temperature room.

The first mixture of gases used was one containing a

Fig. 3.



small proportion of carbon dioxide in hydrogen. Before commencing an experiment the apparatus was washed through with a slow stream of hydrogen for several hours, and then with the mixture of gases until the fringes in the interferometer showed no movement after one hour. During the preliminaries the mercury was not dropping in F.

Then the mercury is allowed to fall from the nozzle. The rate of dropping is determined by observing when the drops appear stationary and properly spaced at the nozzle when stroboscopically examined by means of an "Ashdown Rotoscope." This setting can be made an average for all twenty-five streams, and it can be reproduced to about 1 per cent. In most of the experiments the rate of flow of gas

* Burdon, Proc. Phys. Soc. Lond. xxxviii. p 148 (1926).

was about .24 cubic centimetre per second in each limb of the apparatus, and this remained constant for hours. Some time after commencing dropping the fringes begin to move and attain a constant deflexion after two hours. As this shift became greater than a few fringes, it was compensated by turning the compensating plate of the interferometer. The latter was calibrated for small variations about the particular composition used, so that the percentage composition change can be at once deduced from the fringe shift. By slightly warming the wax joint at P_1 (fig. 1) the collecting-tube could be slipped to one side and the mercury from S allowed to collect for a period of 10 or 20 seconds in a measuring cylinder. From the volume thus collected and the number of drops which have fallen in the period, the volume, and hence the area of a single drop, can be calculated. The total area of mercury surface exposed to the gas per second is therefore known, and the number of molecules adsorbed per square centimetre can be obtained from the other factors in the manner which has been indicated in discussing the method.

Results.

A typical set of observations is tabulated in Table I.

TABLE I.

Atmosphere 2 per cent. CO_2 in H_2 .

Temperature of mercury $16^{\circ}\cdot 1$ C.

Total pressure of gas inside apparatus: 79.0 cm. (P).

Temperature of gas 14° C.¹

Time. (Hrs., mins.)	Rate of flow. (v.)	Rate of dropping. (N.)	Volume of drops in 1 second. (V.)	Composition change (from fringe shift). (O.)
0.0	.24 c.c.	$20\cdot 2 \times 25$	1.54 c.c.	0 %
0.20	—	—	—	.002 „
0.40	.25 „	20.1 „	1.56 „	.033 „
1.0	—	—	—	.198 „
1.20	—	—	—	.371 „
2.0	.24 „	20.1 „	—	.400 „
2.30	—	—	—	.400 „
3.0	.24 „	20.1 „	1.53 „	.400 „
Average	.24 c.c.	$20\cdot 1 \times 25$	1.54 c.c.	Constant change } .400 %

Substitution of these quantities in the equation given earlier gives for the number of molecules of CO_2 adsorbed per square centimetre of mercury surface, at a temperature of $16^{\circ}\cdot 1$ C., from a 2 per-cent. mixture with hydrogen :

$$n = \cdot 5 \times 10^{15}.$$

Similar measurements have been made with $\cdot 5$, 5, 10, and 50 per cent. mixtures of the same gases. The whole of the measurements made on these mixtures are tabulated in Table II.

TABLE II.

Per cent. CO_2 in H_2 .	n .	Temperature.
$\cdot 5$	$\cdot 3 \times 10^{15}$	15° C.
2	$\cdot 5$ „	16 „
5	$\cdot 7$ „	16 „
10	$\cdot 7$ „	$16\cdot 5$ „
50	$\cdot 8$ „	16 „

The observations on the 2-per-cent. and the 5-per-cent. mixtures were repeated on different days and yielded identical results. The others are the result of only one experiment for each concentration, but it should be remembered that the factors which enter into the calculations are verified several times during any one run. Owing to the very much reduced sensitivity of the interferometer at the high concentrations, the last measurement is probably in error by as much as 20 per cent. either way, but it serves to indicate that the layer adsorbed is approximately the same, even at very high concentrations, namely about $\cdot 7 \times 10^{15}$ molecules per square centimetre.

For comparison with these, some experiments were carried out with similar mixtures of CO_2 and the inert gas argon in place of the hydrogen, and the results obtained are tabulated in Table III.

TABLE III.

Per cent. of CO_2 in argon.	n .	Temperature.
5	$\cdot 6 \times 10^{15}$	$14^{\circ}\cdot 5$ C.
10	$\cdot 6$ „	15 „
15	$\cdot 5$ „	16 „

Discussion of Results.

It is evident from the above that at all concentrations above about 2 per cent. carbon dioxide is adsorbed at a mercury surface to give a layer of very nearly the same density, namely between $\cdot 6$ and $\cdot 7 \times 10^{15}$ molecules per square centimetre. The diameter of a molecule of CO_2 , as given in the 'Smithsonian Physical Tables,' is $4 \cdot 2 \times 10^{-8}$ cm.; and if we assume the molecules on the mercury surface to occupy a square with this length of side, then in order to form a monomolecular layer over one square centimetre, $\cdot 6 \times 10^{15}$ molecules (very nearly) would be required. It therefore seems reasonable to assume that a monomolecular layer of CO_2 is normally formed at atmospheric pressure on a freshly-prepared mercury surface in a mixture of this gas with a much less easily condensable gas such as H_2 or argon, provided that the concentration of the CO_2 exceeds about 2 per cent.

The present work definitely establishes that adsorption does take place on an expanding mercury surface, and indicates that the forces involved are quite large, for the gas is retained while mercury drops fall through about 50 cm. It is improbable that the adsorption of this gas has a negligibly small effect on the surface-tension, and hence a method for measuring the surface energy should give very different values in a gas and in a vacuum. As has been pointed out, the "large-drop" method for measuring the surface-tension gives a very high initial value in a gas, which falls rapidly to a value considerably lower than the vacuum value. On the other hand, the "drop-weight" method of Harkins does not show these differences. It therefore seems probable that the values given by the former are more reliable than those given by the latter method. The results obtained by Perucca, who measured the change in the contact potential of a mercury surface against platinum in vacuum and after exposure to various gases, also support the view that the surface energy is very different in the two cases.

In this connexion it might be mentioned that measurements of the surface-tension of water and of aqueous solutions of salt by the capillary rise method, using a special technique for obtaining the height of the meniscus at very short intervals after the surface has been formed, have been made by Kleinmann* and others. These indicate that the

* Kleinmann, *Ann. d. Phys.* lxxx. p. 245 (1926). Schmidt und Steyer, *Ann. d. Phys.* lxxix. (1926).

initial surface-tension in contact with gases in considerably higher than for older surfaces.

These experiments were carried out in the Physical Laboratory of the University of Adelaide during 1927. The departure of the author for England interrupted the work at this stage, but it is hoped to be able to present at a later date further results obtained with a greater range of concentrations and with other gaseous mixtures.

In conclusion, I wish to express my sincere thanks to Mr. R. S. Burdon, to whose inspiration and continued help the success of these experiments is largely due.

XLIV. *Evidence of the Anisotropy of the Carbon Atom.* By KATHLEEN LONSDALE (née YARDLEY), D.Sc.(London), Amy Lady Tate Scholar *.

IN a recent paper⁽¹⁾ the writer has given the results of an X-ray examination into the structures of the fully-halogenated ethane derivatives, and has shown that in the solid state the molecule C_2Cl_6 , for example, has only one plane of symmetry and a pseudo-centre. This one symmetry plane passes through both carbon atoms and two of the halogen atoms, the other four being arranged in pairs at equal distances from the plane.

1. Assuming a truly tetrahedral distribution of the carbon atom valencies, the possible symmetries of the C_2Cl_6 molecule would be :

- (a) C_{3i} (rhombohedral),
- (b) D_3 (trapezohedral),
- (c) D_{3d} (ditrigonal scalenohedral),
- (d) C_{3h} (trigonal bipyramidal),
- (e) D_{3h} (ditrigonal bipyramidal),

according to the symmetry of the chlorine atoms and the relative arrangement of the two carbon atoms.

If, on the other hand, the four carbon valencies are not assumed to be alike, the symmetry of the C_2Cl_6 molecule may be reduced.

2. Assuming that there are three similar A valencies and one B valency, then combination between two similar carbon

* Communicated by Prof. R. Whiddington, F.R.S.

atoms and six similar chlorine atoms could take place in such a way as to give the molecule any of the above symmetries or else one of the following :—

- (a) A plane through both C atoms (*i. e.* parallel to the C—C bond) + a centre of symmetry.
- (b) Two planes, one parallel and one perpendicular to the C—C bond.
- (c) A plane parallel to the C—C bond (+ a pseudo-plane perpendicular to the bond).
- (d) A plane parallel to the C—C bond (+ a pseudo-centre).
- (e) A plane perpendicular to the C—C bond.
- (f) A dyad axis perpendicular to the C—C bond (+ a pseudo-plane perpendicular to the bond).
- (g) A dyad axis perpendicular to the C—C bond (+ a pseudo-centre).
- (h) A dyad axis perpendicular to the C—C bond (no pseudo-symmetry).
- (i) A centre of symmetry.
- (j) No symmetry.

It will be seen that one of these, (d), corresponds to the symmetry actually found.

3. Assuming that there are two similar A valencies and two similar B valencies in the carbon atom, then the C_2Cl_6 molecule might possess any of the symmetries (a)—(j) given for 2.

4. The same symmetries could exist if only two of the four carbon valencies were alike.

If all the carbon valencies were different, the C_2Cl_6 could only have one of the symmetries 2 (f)—2 (j). Experimental evidence, so far as this particular group is concerned, therefore points to the arrangement (d), or 4 (d), in which the molecules would be as in fig. 1.

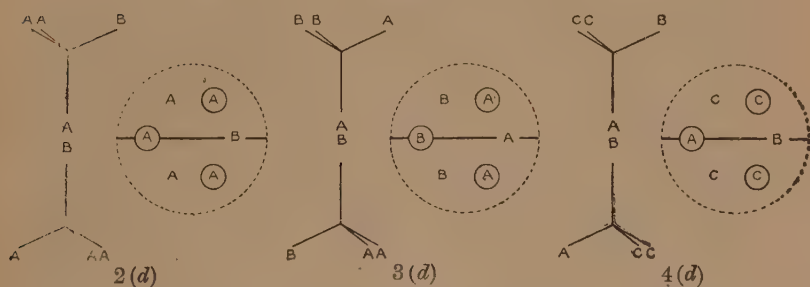
The single bond between the carbon atoms is an actual sharing of two unlike valencies.

It has been pointed out that this crystallographic evidence shows that the A, B, etc. valencies must be different in a geometrical sense, although such a difference probably implies further differences in chemical properties. It is possible that the difference is due to the presence of very heavy or extensive groups

are attached to a carbon atom the lack of symmetry of the carbon atom might easily be either masked or enhanced. There is a considerable amount of evidence, however, from other fields of work pointing to an anisotropy of the carbon atom.

In 1923 Main Smith⁽²⁾ published a table giving extra-nuclear electronic configurations based on chemical considerations. According to his arrangement two of the outer electrons of neutral carbon would occupy (2, 1) orbits and the remaining two (2, 2) orbits. In 1924 Fowler⁽³⁾ showed that the emission spectrum of $C+$ ($CII.$) is similar to that of $B(BI.)$, and concluded therefore that their electronic arrangements are similar; that is, that of the three outer electrons in $C+$, two move in (2, 2) orbits, while the electron which generates the spectrum traverses

Fig. 1.



a (2, 1) orbit. Independently of Main Smith, Stoner⁽⁴⁾ compiled a table similar to his, based principally on such spectroscopic evidence. The structure of neutral carbon was fully confirmed the following year by Millikan and Bowen⁽⁵⁾, who examined carbon spectroscopically as $C+$, $C++$, $C+++$, and showed conclusively that in neutral carbon there are two (2, 2) and two (2, 1) electrons.

This evidence shows that in all probability the carbon atom is of the type 3, possessing two A and two B electrons, rather than of the other geometrically possible types 2 or 4. These A and B valencies must surely be closely related to the existence of the two (2, 2) and two (2, 1) electrons in the neutral atom.

The structure of methane and of its derivatives has occupied considerable attention on the part of various workers. Methane crystallizes in the cubic system below

$-185^{\circ}8\text{ C.}$, but at a lower temperature still there is an enantiotropic transition into a doubly-refracting modification⁽⁶⁾. Similarly CCl_4 , which is cubic below -22° C. , becomes doubly-refracting at -47° C. ⁽⁷⁾, being presumably isomorphous with CBr_4 , which is cubic above 46° C. but monoclinic (pseudo-cubic) below that temperature⁽⁸⁾. Bridgeman⁽⁹⁾ has found three solid modifications of CCl_4 and of CBr_4 , one stable at atmospheric pressures (the regular form) and the other two at considerably higher pressures. This indicates that the useful symmetry of the carbon atom, in combination with other atoms in the solid state, may vary with temperature and pressure.

No complete X-ray analysis of the crystal structure has yet been given for any of these substances, but Mark⁽¹⁰⁾ has investigated the regular modifications of CBr_4 and Cl_4 by means of the powder method, and has placed them in the space-group T_d^1 (hexakis-tetrahedral), there being apparently one molecule in a unit cell, of side $5.67\text{ \AA.}$ in the case of CBr_4 , and $5.81\text{ \AA.}$ in the case of Cl_4 . For monoclinic CBr_4 , Mark found that the unit cell contained eight atoms of carbon and thirty-two of bromine, so that presumably polymerization had taken place, the molecule being at least C_2Br_8 . $\text{C}(\text{NO}_2)_4$, $\text{C}(\text{CH}_3)_4$ are also cubic⁽¹¹⁾ with low temperature doubly-refracting modifications. The regular forms of both of these have been examined by means of X-rays⁽¹²⁾. The molecule $\text{C}(\text{NO}_2)_4$ appears to possess trigonal symmetry, one NO_2 group being unique; $\text{C}(\text{CH}_3)_4$ possesses probable molecular symmetry T_d . Other symmetrically substituted methane derivatives crystallize with tetragonal or lower symmetry⁽¹³⁾. In 1923 Mark and Weissenberg⁽¹⁴⁾ published an X-ray examination of pentaerythritol, $\text{C}(\text{CH}_2\text{OH})_4$, the results of which (supposedly confirmed by Huggins and Hendricks⁽¹⁵⁾) have aroused much interest and controversy. These authors accepted the class C_{4v} given by Martin⁽¹⁶⁾, being unaware that Haga and Jaeger⁽¹⁷⁾ had shown by means of an excellent Laue photograph that the planes of symmetry supposed to intersect in the tetrad axis were non-existent. Various papers referring to this point followed^{(18), (19)}. X-rays can, in general, give no evidence as to the polarity of a crystal. Mark and Weissenberg assumed, after Martin, that pentaerythritol is polar, and then showed that in that case the only possible symmetry of the $\text{C}(\text{CH}_2\text{OH})_4$ molecule is C_4 . Thus the molecule would be of a pyramidal shape, the four valency directions of the carbon atom pointing along the edges of a tetragonal pyramid. Liebisch⁽²⁰⁾ had affirmed that the

pyro-electric test gave positive results for these crystals, and Giebe and Scheibe⁽²¹⁾ had recorded a positive result for the piezo-electric test. Armed with this evidence Weissenberg⁽²²⁾ and Reis⁽²³⁾ developed a new stereochemistry for the carbon atom, based on its possible non-tetrahedral form. Mark and Weissenberg's conclusions have not, however, remained unchallenged. I. Nitta⁽²⁴⁾ has repeated the X-ray investigation, and has shown that the results obtained are consistent with either a pyramidal (C_4) or a sphenoidal (S_4) symmetry of the $C(CH_2OH)_4$ molecule. This result has been confirmed by S. B. Hendricks⁽²⁵⁾ and by A. Nehmitz⁽²⁶⁾. The latter believes that the X-ray intensities observed favour the sphenoidal symmetry. On the purely crystallographic side I. E. Knaggs (*loc. cit.*) and later Schleede and Schneider⁽²⁷⁾ have been unable to detect any evidence of polarity in the crystal habit or by means of etch figures. Schleede and Schneider grew a number of crystals which appeared to show definite S_4 symmetry, the basal faces (001) and (00 $\bar{1}$) being rectangles whose long sides were crossed. Finally, H. Siefert⁽²⁸⁾ has very carefully reinvestigated the crystallographic properties of pentaerythritol. He obtained crystals which closely simulated C_{4h} symmetry, but which might have been formed by twinning of a lower class of symmetry. By cutting sections parallel to (001) at both ends of these bipyramids and etching on each of the four faces so obtained, he was able to prove that the bipyramids were formed of two interpenetrating bisphenoids and that the true crystal class is S_4 . He remarks that he obtained an apparent pyroelectric effect with the crystals, but that, since true pyroelectricity is impossible in the bisphenoidal class, the effect is probably only a manifestation of the piezo-electric effect, and quotes, in this connexion, the example of quartz (see R. E. Gibbs, *Science Progress*, lxxxviii. p. 613 (1928), for a brief summary of the properties of quartz), for which the existence of a true pyroelectric effect is also doubtful. Hettich and Schleede⁽²⁹⁾ have shown that piezo-electricity is compatible with S_4 symmetry, since its presence only indicates a lack of centro-symmetry.

Cooley⁽³⁰⁾ examined the fine structure of the band spectrum of methane, and found for the band at approximately 3.31μ , $\frac{\Delta}{\lambda} = 9.77 \text{ cm.}^{-1}$, whereas for the band at 7.7μ , $\frac{\Delta}{\lambda} = 5.41 \text{ cm.}^{-1}$. Dennison⁽³¹⁾ discussed these results on the basis of a tetrahedral molecule, and showed that the

observed difference in $\frac{\Delta}{\lambda}$ for the two bands may possibly be explained by the assumption that the CH_4 molecule possesses a resultant angular momentum fixed in direction in the molecule of the amount $\frac{1}{2}\left(\frac{h}{2\pi}\right)$. Guillemin⁽³²⁾, however, used Cooley's results to calculate the potential energies, (1) of a tetrahedral CH_4 molecule, and (2) of a pyramidal CH_4 molecule, and came to the conclusion that the pyramidal arrangement would be the more stable of the two. He assumed that the carbon was $-^{\text{ve}}$ (and therefore polarizable) and the hydrogens $+^{\text{ve}}$, an hypothesis which is by no means justified. He also accepted Grimm's⁽³³⁾ value of the CH_4 radius, which is about 10^{-8} cm., whereas Wasastjerna⁽³⁴⁾, whose calculations for other atoms have been fully confirmed by the latest X-ray results, gives as the radius of Kr, and therefore approximately of CH_4 , the value 1.76 Å. For CCl_4 , however, the tetrahedral arrangement is considered to be the more stable, and Guillemin suggests that a change from the pyramidal to the tetrahedral configuration may take place on substitution. Havelock⁽³⁵⁾ has used Guillemin's figures for the C—H distance to calculate the molecular refractivity and depolarization factors on the basis of a tetrahedral and a pyramidal arrangement of the methane molecule. In each case the values found are smaller than the experimental values, and Havelock suggests that is because Guillemin's figures are too small. Van Arkel and de Boer⁽³⁶⁾, independently of Guillemin, have made calculations for a CH_4 molecule in which the hydrogens, being $-^{\text{ve}}$, are polarizable, and the carbon is $+^{\text{ve}}$, and they have shown that the tetrahedral form is the more stable, both for CH_4 and also for CCl_4 .

Carbon tetraphenyl forms rather poor crystals, and its symmetry is not yet fully ascertained. Wahi⁽³⁷⁾ has placed it in the orthorhombic system as the result of an examination of its optical properties. W. H. George⁽³⁸⁾ has examined it by X-ray photographic methods, and has shown that the structure approximates closely to the tetragonal space-group D_{2d}^4 . The molecular symmetry is either S_4 or a close approximation to it. No other crystalline modification has been found at temperatures above -200°C .

Gerstacker, Moller, and Reis⁽³⁹⁾ have examined the compounds penta-erythritol tetra-nitrate and penta-erythritol tetra-acetate. They place the first in the space-group D_{2d}^4 and the second in C_{4h}^3 , with two molecules per unit cell in each case. The former compound could therefore only have

S_4 symmetry and the latter C_1 or S_4 symmetry. They give reasons, based on the crystal habit, for believing that the molecules of penta-erythritol tetra-acetate are pyramidal. I. E. Knaggs, however, has subsequently pointed out⁽⁴⁰⁾ that the space-group of the latter substance is most probably not C_{4h}^3 . Her examination of the crystals by ionization and by photographic methods failed to reveal any trace of odd orders of (001), and thus pointed to C_{4h}^4 as the true space-group and to S_4 as the only possible molecular symmetry. The writer, at Miss Knaggs's request, also examined the crucial plane very carefully by the ionization method, and confirmed the absence of odd order reflexions. It appears, therefore, that no case of a pyramidal arrangement of the carbon valencies has as yet been satisfactorily substantiated. The X-ray results so far obtained indicate that the carbon atom may be tetrahedral, trigonal, sphenoidal, or a close approximation to one of these symmetries.

Ebert and von Hartel⁽⁴¹⁾ have shown that many compounds of the type C_{a4} , such as $C(OCH_3)_4$, $C(OC_2H_5)_4$, $C(CH_2 \cdot O_2C \cdot CH_3)_4$, have measurable dielectric orientational polarizations in dilute benzene solution, and they have calculated the dipole moments of the molecules. They and Weissenberg⁽⁴²⁾ take these positive results as proof of the pyramidal structure of the molecules in question. It should be pointed out, however, that the existence of a dipole moment only shows that the molecules are not truly tetrahedral. It is difficult to see how they can even be truly sphenoidal, as indicated (in the case of $C(CH_2 \cdot O_2C \cdot CH_3)_4$) by the X-ray results. A carbon atom of the type postulated by the writer, having two A and two B valencies, would, however, possess a small dipole moment, which would probably be greater the more "elongated" the substituted groups. Williams and Krehma⁽⁴³⁾ have shown that the dipole moment of CCl_4 is negligible.

Further evidence for the anisotropy of the carbon atom comes from a consideration of the polarization factor for light scattered by methane, tetrachlormethane, etc. According to theory, if these substances were completely isotropic the depolarization factor should be zero. Cabannes and his collaborators^{(44), (45)} and Rayleigh⁽⁴⁶⁾ have found a small depolarization factor, even for the rare-gas atoms He, Ne, A, Kr, Xe; for CH_4 Cabannes found⁽⁴⁷⁾ $\rho = 0.015$ and for CCl_4 ⁽⁴⁸⁾ $\rho = 0.0087$. Other investigators^{(49), (50), (51)} have obtained higher values for CCl_4 , but Cabannes is the only worker who has given results for both, and he states that the depolarization factor is definitely bigger for CH_4 .

than for CCl_4 . This he takes as conclusive proof that it is really the carbon atom which is anisotropic, since when the less refringent atoms of hydrogen are replaced by the much more refringent atoms of chlorine, the relative importance of the carbon atom and the consequent degree of anisotropy of the molecule will therefore be diminished.

A summary of much of the work in this and other fields has been given by V. Henri⁽⁵²⁾, who, however, has quoted Cabannes's results in support of Guillemin's pyramidal model for CH_4 and tetrahedral model for CCl_4 .

Application to Simple Crystal Structures.

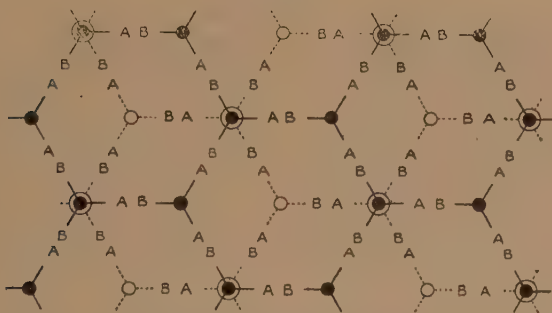
It is of interest to see how such a carbon atom as that suggested by the X-ray work on the C_2Cl_6 series, having two A and two B valencies, will fit in with the X-ray results for other carbon compounds. Diamond, of course, suggests itself first. Grimm and Sommerfeld⁽⁵³⁾ have pointed out that C, Si, Ge, and Sn all crystallize in the diamond type of lattice, and that, according to the Main Smith-Stoner classification, each of these contains two complete sub-groups of two electrons each, and requires an extra four electrons in order to reach the (2, 2, 4) grouping characteristic of the inert gases. The suggestion implied, that the electronic configuration must be similar in each of these crystalline substances, has been vigorously attacked by Hume-Rothery⁽⁵⁴⁾, who points out, however, that in diamond itself all the properties of the crystal indicate that the forces joining the carbon atoms in the lattice closely resemble those which bind together the atoms of a molecule. Thus the diamond is extremely hard, infusible below 3000°C ., and possesses a specific resistance of about 10^{+14} ohm-cm. The present writer⁽⁵⁵⁾ has shown that if C—C bonds in diamond are taken to resemble that in the molecule C_2Cl_6 , the cubic symmetry may be explained on the assumption that the (AB) electrons forming or contributing to the bond are absolutely mutually shared by the two carbon atoms in question. Carbon atoms of the AAAB or ABCC types referred to earlier could not fit into a strictly cubic lattice of the dimensions found, and even if a larger unit cell were assumed, the bonds linking the atoms together would not be all of one kind.

Graphite is a more difficult problem. The accepted structure, given independently by Hassel and Mark⁽⁵⁶⁾ and by Bernal⁽⁵⁷⁾, is one in which the carbon atoms lie in planes in which they form hexagonal nets. Half the atoms in one net lie normally above half the atoms of a net in the plane

beneath, while the other half lie normally above the centres of the hexagons of this net. Alternate nets lie atom for atom normally above each other. The tetrahedral symmetry of the carbon atom is thus lost, three of the valency directions lying in one plane, while the fourth is directed apparently at right angles to this plane. As Bernal points out, this result is inevitable in any graphite structure. Cleavage sheets of graphite possess considerable hardness and tenacity in their own plane, and it is therefore justifiable to assume that the linking between carbon atoms *in* this plane is similar to that in diamond (fig. 2), consisting entirely of (AB) junctions.

If the sharing is mutual, that is, if an (AB) junction is exactly equivalent to a (BA) junction, then the nets will be truly hexagonal. Bernal mentions a further difficulty,

Fig. 2.

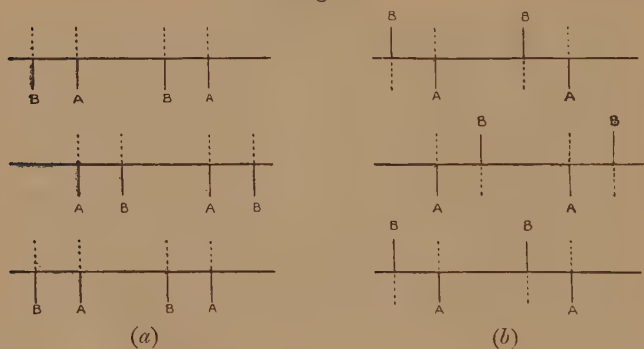


which is that the carbon atoms in graphite fall into two classes, according as to whether their nearest neighbours along the [0001] direction are at a distance 3.41 or 6.82 Å., and, moreover, even the distance 3.41 is extremely large compared with the normal C—C distance (1.54 Å. in diamond, 1.42 Å. in the graphite cleavage planes). These difficulties are capable of explanation if the structure given in fig. 2 is correct; the projection of the structure on a plane at right angles to that of fig. 2 is shown in fig. 3 (a) or (b). The two types of carbon atoms are now clearly seen to be those which have an A-valency direction normal to the cleavage plane and those which have a B-valency direction normal (or possibly inclined) to that plane.

It is not known to what class graphite belongs, and therefore the space-group cannot definitely be fixed. Hassel and Mark give a list of possible space-groups, reducing them by means of arguments based on observed intensities.

Laue photographs and X-ray methods in general cannot distinguish between the classes D_{3h} , C_6 , D_6 , and C_{6h} . Hence it is impossible to say whether graphite is polar or non-polar. If it is non-polar, then the fourth valency or electron orbit must somehow be symmetrical about the cleavage plane. This is indicated by the dotted lines in the diagrams. The argument, of course, applies to any graphite structure. The junctions between atoms in successive cleavage planes are likely to be extremely weak, and, in fact, half of the carbon atoms may practically be regarded as unsaturated. Hence, probably, the ease with which graphite can combine with hydrogen to form a weak chemical compound and the tendency of various atoms to attach themselves to the surface of charcoal (which is hydrogenated graphite in a fine state of division).

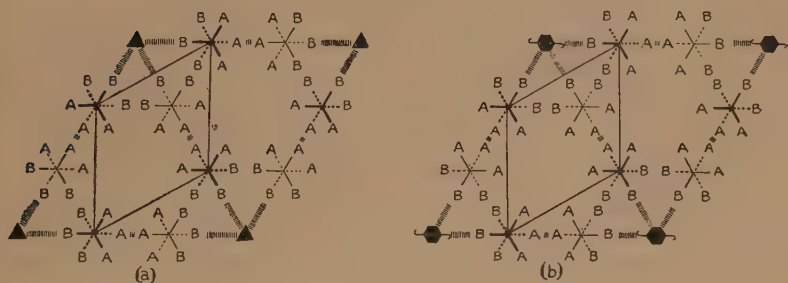
Fig. 3.



Another substance the crystal structure of which requires a closer investigation is ethane, C_2H_6 . Wahl showed⁽⁵⁸⁾ by the optical behaviour and the rhombohedral cleavage that at the temperature of liquid air ethane crystallizes in the hexagonal system. Mark and Pohland⁽⁵⁹⁾ pursued the investigation by means of the X-ray powder method, and showed that the unit cell, of size $4.462 \times 8.193 \text{ \AA}$, contains two molecules, characteristic points of which are approximately in the "close-packed" positions. The C—C bond lies along the principal axis, the distance between the carbons of one molecule being about $1.55 \text{ \AA}$. The positions of the H atoms could not be located. Niven⁽⁶⁰⁾ has suggested that in C_2H_6 all the (2, 2) electrons and two of the (2, 1) electrons of the carbon atoms are taken by the six hydrogen atoms to complete their (1, 1) orbits, while the remaining two (2, 1) electrons form a closed system of

two, thus making a bond between the two C atoms. If, as is almost certain, however, ethane is similar to hexachlor-ethane in the arrangement of the carbon valencies, the bond between the two C atoms would be formed by two unlike valencies. We must therefore see how such a molecule, having a plane through the two C atoms and two of the H atoms, together with a pseudo-centre, will fit into the structure recorded by Mark and Pohland. It is found, by examining every geometrical possibility, that in order to retain the hexagonal symmetry the unit cell must be at least three times the volume of that given by Mark and Pohland. This is not incompatible with their results, for they themselves say that the method they used was not sufficiently accurate to exclude the possibility of a unit cell larger than that given in their paper. Two possible

Fig. 4.



structures then present themselves, either of which is in agreement with the results found (fig. 4 (a) and (b)).

The cell indicated by the powder method is shown by full lines. The height of the cell remains unchanged, but its dimensions are now

$$(4.46 \times \sqrt{3})^2 \times 8.19 \text{ \AA.}^3,$$

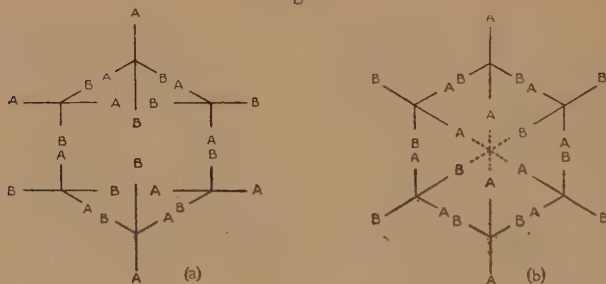
and it contains six molecules, each possessing a plane of symmetry.

In the case (a) no reflexion would be really absent, but planes of indices ($mm\bar{2}ml$) where l is odd (referred to the cell given by Mark and Pohland) would have negligible odd orders. In the case (b) those orders would actually be absent. [In the true cell this would correspond to a halving of planes ($m0\bar{m}l$) where l is odd.] Now an examination of the experimental results shows that only one such reflexion is recorded, that from $(11\bar{2}3)$, and even this weak reflexion

is very doubtful, since it coincides well within the limits of experimental error (given as 3 per cent.) with the reflexion from the (2022) plane. Until experimental data of much greater accuracy can be obtained using single crystals of ethane, it is not possible to say which of the above structures, if either, is true to the facts.

Another hydrocarbon which is of even greater importance is benzene. Unfortunately, X-ray results relating to crystalline benzene are most incomplete. Broomé⁽⁶¹⁾ has used powder and Laue methods to show that the unit orthorhombic cell contains four molecules, and Mark⁽⁶²⁾ quotes a dissertation by Schneefusz (Berlin, 1924—not available to the writer) in which the dimensions are verified and the space-group is given as Q_h^{11} , Q_h^{15} , Q_h^{16} , the molecule being apparently centro-symmetrical. Schneefusz has also

Fig. 5.



used X-ray methods to prove that C_6Cl_6 , C_6Br_6 , and C_6I_6 are centro-symmetrical, crystallizing in the monoclinic system. Similar results for C_6Cl_6 and C_6Br_6 were arrived at independently by Plummer⁽⁶³⁾. If the benzene ring of six carbon atoms persists with more or less distortion just as it exists in diamond or graphite, then again we must expect that the C—C bonds will consist of (AB) junctions. The existence of centro-symmetry definitely eliminates the Kekulé model with its three double bonds. Centro-symmetrical models, having no further symmetry, may be built up either on the Ladenburg or the Armstrong-Baeyer models (fig. 5 (a) and (b)).

By an extension of the fourth (internal) valencies, so that actual linking takes place within the ring, fig. 5 (b) could be made to represent the Claus model.

In conclusion, it may be stated that the structure here suggested for the carbon atom, in which two of the valencies are geometrically different from the other two, agrees with

the crystallographic determinations on various substances as least as well as, if not better than, the ordinary tetrahedral model, and is able to explain the curious lack of symmetry of many simple carbon compounds.

The writer wishes to express her indebtedness to the Council of Bedford College, London, for a scholarship enabling her to carry on research work at the University of Leeds.

Summary.

The possible symmetry of the carbon atom is investigated in the light of X-ray results on crystals of C_2Cl_6 and isomorphous compounds. A model is obtained having two A and two B valencies, geometrically different, and a comparison is made with the Main Smith-Stoner atom. Work in other fields is also quoted in favour of a non-tetrahedral carbon atom. A critical account is given of the controversy concerning pentaerythritol and other symmetrically substituted derivatives of methane, and it is shown that no case of a pyramidal carbon atom has yet been satisfactorily proved. It is found that the model now suggested will explain the symmetries, as determined by means of X-rays, of other simple carbon compounds, in some cases throwing light on anomalies revealed by such determinations.

References.

- (1) K. Yardley, *Proc. Roy. Soc. A*, cxviii. p. 449 (1928).
- (2) J. D. Main Smith, *Journ. Soc. Chem. Ind. (Chem. and Ind. Rev.)* xliii. p. 323 (1923).
- (3) A. Fowler, *Proc. Roy. Soc. A*, cv. p. 299 (1924).
- (4) E. C. Stoner, *Phil. Mag.* xlviii. p. 719 (1924).
- (5) R. A. Millikan and I. S. Bowen, *Phys. Rev.* xxvi. pp. 150, 310 (1925).
- (6) W. Wahl, *Proc. Roy. Soc. A*, lxxxvii. p. 377 (1912); xc. p. 1 (1914).
- (7) W. Wahl, *Proc. Roy. Soc. A*, lxxxix. p. 330 (1913).
- (8) — Zirngiebl. See P. Groth, *Chem. Kryst.* i. p. 230.
- (9) P. W. Bridgeman, *Phys. Rev.* iii. p. 153 (1914).
- (10) H. Mark, *Ber. Deut. Chem. Ges.* lvii. p. 1820 (1924).
- (11) W. Wahl, *Proc. Roy. Soc. A*, lxxxix. p. 333 (1913); lxxxviii. p. 359 (1913).
- (12) H. Mark and W. Noethling, *Zeit. f. Krist.* lxxv. p. 442 (1927).
- (13) I. E. Knaggs, *Trans. Chem. Soc.* cxxiii. p. 71 (1923).
- (14) H. Mark and K. Weissenberg, *Zeit. f. Phys.* xvii. p. 301 (1923).
- (15) M. L. Huggins and S. B. Hendricks, *Journ. Am. Chem. Soc.* xlviii. p. 164 (1926).
- (16) J. Martin, *Neues Jahrbuch f. Min.* vii. p. 1 (1890); cf. P. Groth, *Chem. Kryst.* iii. p. 385.
- (17) H. Haga and F. M. Jaeger, *Proc. Kon. Akad. Wetensch. Amst.* xviii. p. 1350 (1916).

- (18) H. G. Westenbrink and F. A. van Melle, *Zeit. f. Krist.* lxiv. p. 548 (1926).
- (19) H. Mark and K. Weissenberg, *Zeit. f. Krist.* lxv. p. 499 (1927).
- (20) T. Liebisch, *Grundriss der Phys. Kryst. Leipzig*, p. 141 (1896).
- (21) E. Giebe and A. Scheibe, *Zeit. f. Phys.* xxxiii. p. 760 (1925).
- (22) K. Weissenberg, *Ber. d. Deut. Chem. Ges.* lix. p. 1526 (1926); cf. H. Mark and K. Weissenberg, *Zeit. f. Phys.* xlvii. p. 301 (1928).
- (23) A. Reis, *Ber. Deut. Chem. Ges.* lix. p. 1543 (1926).
- (24) I. Nitta, *Bull. Chem. Soc. Japan*, i. p. 62 (1927).
- (25) S. B. Hendricks, *Zeit. f. Krist.* lxvi. p. 131 (1927).
- (26) A. Nehmitz, *Zeit. f. Krist.* lxvi. p. 408 (1928).
- (27) A. Schleede and E. Schneider, *Naturwissenschaften*, xv. p. 970 (1927).
- (28) H. Siefert, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, p. 289 (1927).
- (29) A. Hettich and A. Schleede, *Zeit. f. Phys.* xlv. p. 147 (1927).
- (30) J. P. Cooley, *Astrophys. Journ.* lxii. p. 73 (1925).
- (31) D. M. Dennison, *Astrophys. Journ.* lxii. p. 84 (1925).
- (32) V. Guillemin, jun., *Ann. der Phys.* lxxxi. p. 173 (1926).
- (33) H. G. Grimm, *Zeit. f. Electrochemie*, xxxi. 474 (1925).
- (34) J. A. Wasastjerna, *Comm. Phys.-Math. Soc. Scient. Fennicæ*, i. p. 38 (1923).
- (35) T. H. Havelock, *Phil. Mag.* iii. p. 433 (1927).
- (36) A. E. van Arkel and J. H. de Boer, *Zeit. f. Phys.* xli. pp. 27, 38 (1927).
- (37) W. Wahl, *Zeit. f. Phys. Chem.* lxxxviii. p. 129 (1914).
- (38) W. H. George, *Proc. Roy. Soc. A*, cxiii. p. 585 (1927).
- (39) A. Gerstäcker, H. Möller, and A. Reis, *Zeit. f. Krist.* lxvi. p. 355 (1928).
- (40) I. E. Knaggs, 'Nature', cxxi. p. 616 (1928).
- (41) L. Ebert and H. von Hartel, *Naturwissenschaften*, xv. p. 669 (1927).
- (42) K. Weissenberg, *Naturwissenschaften*, xv. p. 662 (1927).
- (43) J. W. Williams and I. J. Krehma, *Journ. Am. Chem. Soc.* xlix. p. 1676 (1927).
- (44) J. Cabannes, *Ann. de Phys.* xv. p. 120 (1921).
- (45) J. Cabannes and A. Lepape, *Comptes Rendus*, clxxix. p. 326 (1924).
- (46) Lord Rayleigh, *Proc. Roy. Soc. A*, xcviii. p. 57 (1920).
- (47) J. Cabannes and J. Gauzit, *Journ. de Phys.* vi. p. 182 (1925).
- (48) J. Cabannes, *Journ. de Phys.* vii. p. 343 (1926).
- (49) Lord Rayleigh (Hon. R. J. Strutt), *Proc. Roy. Soc. A*, xcv. p. 155 (1919) (material of doubtful purity).
- (50) C. V. Raman and K. S. Rao, *Phil. Mag.* xlv. p. 625 (1923).
- (51) A. S. Ganesan, *Phil. Mag.* xlix. p. 1216 (1925).
- (52) V. Henri, *Chem. Rev.* iv. p. 189 (1927).
- (53) H. G. Grimm and A. Sommerfeld, *Zeit. f. Phys.* xxxvi. p. 36 (1926).
- (54) W. Hume-Rothery, *Phil. Mag.* iii. p. 301 (1927).
- (55) K. Yardley, *loc. cit.*
- (56) O. Hassel and H. Mark, *Zeit. f. Phys.* xxv. p. 317 (1924).
- (57) J. D. Bernal, *Proc. Roy. Soc. A*, cvi. p. 749 (1924).
- (58) W. Wahl, *Proc. Roy. Soc. A*, lxxxviii. p. 354 (1913).
- (59) H. Mark and E. Pohlman, *Zeit. f. Krist.* lxii. p. 103 (1925).
- (60) C. D. Niven, *Phil. Mag.* iii. p. 314 (1927).
- (61) B. Broomé, *Phys. Zeit.* xxiv. p. 124 (1923); *Zeit. f. Krist.* lxii. p. 325 (1925).
- (62) H. Mark, *Ber. d. Deut. Chem. Ges.* lvii. p. 1820 (1924).
- (63) W. G. Plummer, *Phil. Mag.* i. p. 1214 (1925).

XLV. *On the Radiation from the Inside of a Circular Cylinder.*—Part II. By H. BUCKLEY, M.Sc., F.Inst.P.
(From the National Physical Laboratory *.)

IN the Philosophical Magazine for October 1927 † it was shown that the radiation per unit area from the inside of a uniformly heated infinite circular cylinder at temperature T^0 , taking into account multiple reflexions, was given by an integral equation of the form

$$\Phi(x_1) = \epsilon \sigma T^4 + \frac{1-\epsilon}{4} \left\{ \int_0^{x_1} \Phi(x) \frac{d^2}{dx^2} F(x_1-x) dx + \int_{x_1}^{\infty} \Phi(x) \frac{d^2}{dx^2} F(x-x_1) dx \right\},$$

where x and x_1 are measured from the end of the cylinder in terms of the radius, ϵ is the emissivity of the walls, and $\pi/2 \cdot F(x)$ is the radiation from a disk of radius unity and brightness unity to a parallel coaxial disk of radius unity at a distance x away, where

$$F(x) = \{x^2 + 2 - x(x^2 + 4)^{\frac{1}{2}}\}.$$

This equation merely expresses the fact that the radiation from any point of the cylinder is equal to the directly emitted radiation plus the reflected portion of the radiation received from the rest of the cylinder. Solutions of this equation were obtained by taking an approximation to the kernel $\frac{1}{2} \frac{d^2}{dx^2} F(x)$ in the form $\sum_1^n B_n e^{\beta_n x}$, where all the β 's are negative ‡. The approximation was also adjusted so that

$$\int_0^{\infty} \frac{1}{2} \frac{d^2}{dx^2} F(x) dx = \int_0^{\infty} \sum_1^n B_n e^{\beta_n x} dx = 1,$$

$$i. e., \quad \sum_1^n (B_n / \beta_n) = -1.$$

The case considered was when $n=2$, but the extension to higher values of n is easily made and is obvious. It was also shown that for values of the emissivity greater than 0.25 (*i. e.*, reflectivity less than 0.75) the approximate solution obtained with $n=2$ was quite satisfactory and that

* Communicated by Sir J. E. Petavel, K.C.B., F.R.S.

† Buckley, Phil. Mag. iv. p. 753 (1927).

‡ Whittaker, Proc. Roy. Soc. cxiv. p. 367 (1918).

even with $n=1$ the approximation was quite good. The approximate expressions for the kernel were

$$\frac{1}{2} \frac{d^2}{dx^2} F(x) = e^{-x} \quad \text{for } n=1$$

and $\frac{1}{2} \frac{d^2}{dx^2} F(x) = 1.21e^{-1.14x} - 0.21e^{-3.40x} \quad \text{for } n=2.$

The solutions in these cases were found to be

$$\Phi(x) = 1 + A_1 e^{a_1 x} + A_2 e^{a_2 x}$$

and $\Phi(x) = 1 - (1 - \sqrt{\epsilon}) e^{-\sqrt{\epsilon} x},$

where each side has been divided by σT^4 .

It is the purpose of this paper to consider the case of a finite cylinder, and also to apply the results obtained to deduce the brightness of the inside of a non-radiating diffusing cylinder of reflectivity ρ when illuminated by an infinite plane of brightness B and reflectivity zero at an infinite distance from the end of the cylinder. This is the problem of the brightness of a vertical circular shaft or light well illuminated by a uniform sky.

A solution is also obtained of the problem of the radiation from the inside of an infinite circular cylinder which has an infinite longitudinal slit parallel to the axis. This problem is of interest, since it approximates to the platinum black body primary standard of light employed by Ives *, except that emission and reflexion are considered to be perfectly diffuse instead of specular. In this case the solution is exact.

The Finite Radiating Cylinder.

The equation to be solved is

$$\Phi(x_1) = \epsilon + \frac{1-\epsilon}{2} \left[\int_0^{x_1} \Phi(x) \{ B_1 e^{\beta_1(x_1-x)} + B_2 e^{\beta_2(x_1-x)} \} dx \right. \\ \left. + \int_{x_1}^l \Phi(x) \{ B_1 e^{\beta_1(x-x_1)} + B_2 e^{\beta_2(x-x_1)} \} dx \right],$$

where l is the length of the cylinder. It is obvious that the solution will be symmetrical about the mid-point of the cylinder, so that

$$\Phi(x) = \Phi(l-x).$$

This suggests that $\Phi(x)$ is of the form

$$\Phi(x) = A_0 + A_1 e^{a_1 x} + A_1 e^{a_1(l-x)} + A_2 e^{a_2 x} + A_2 e^{a_2(l-x)}.$$

* Ives, Journ. Frank. Inst. cxvii. pp. 147, 359 (1924).

On substituting this expression in the equation above, performing the integrations and equating the constant terms and the coefficients of $e^{\alpha_1 x_1}$, $e^{\alpha_2 x_1}$, $e^{\beta_1 x_1}$, and $e^{\beta_2 x_1}$ on each side of the equation, it is found that

$$A_0 = \epsilon - A_0(1 - \epsilon) \left(\frac{B_1}{\beta_1} + \frac{B_2}{\beta_2} \right),$$

$$1 = (1 - \epsilon) \left\{ \frac{B_1 \beta_1}{\alpha_1^2 - \beta_1^2} + \frac{B_2 \beta_2}{\alpha_1^2 - \beta_2^2} \right\},$$

$$1 = (1 - \epsilon) \left\{ \frac{B_1 \beta_1}{\alpha_2^2 - \beta_1^2} + \frac{B_2 \beta_2}{\alpha_2^2 - \beta_2^2} \right\},$$

$$0 = \frac{A_0}{\beta_1} - \frac{A_1}{\alpha_1 - \beta_1} - \frac{A_2}{\alpha_2 - \beta_1} + \frac{A_1 e^{\alpha_1 l}}{\alpha_1 + \beta_1} + \frac{A_2 e^{\alpha_2 l}}{\alpha_2 + \beta_1},$$

$$0 = \frac{A_0}{\beta_2} - \frac{A_1}{\alpha_1 - \beta_2} - \frac{A_2}{\alpha_2 - \beta_2} + \frac{A_1 e^{\alpha_1 l}}{\alpha_1 + \beta_2} + \frac{A_2 e^{\alpha_2 l}}{\alpha_2 + \beta_2}.$$

Four identical expressions are found from the coefficients of $e^{\alpha_1(l-x_1)}$, $e^{\alpha_2(l-x_1)}$, $e^{\beta_1(l-x_1)}$, and $e^{\beta_2(l-x_1)}$, as is to be expected. Furthermore, for $l \rightarrow \infty$ these equations become identical with those obtained in the previous paper for the case of the infinite cylinder.

The first of these equations gives $A_0 = 1$, since

$$\frac{B_1}{\beta_1} + \frac{B_2}{\beta_2} = -1.$$

The second and third show that α_1 and α_2 are given by the square roots of the roots of the quadratic in z ,

$$1 = (1 - \epsilon) \left\{ \frac{B_1 \beta_1}{z - \beta_1^2} + \frac{B_2 \beta_2}{z - \beta_2^2} \right\},$$

which is independent of l , so that the indices of the exponential terms in the solution for the finite cylinder are the same as those for the infinite cylinder. It can also be shown that $\epsilon_1 \alpha_2 = \sqrt{\epsilon} \beta_1 \beta_2$.

The coefficients, however, are different, and are given by the fourth and fifth equations when the values of α_1 and α_2 are substituted in them.

The numerical values of the approximate solutions for $n = 2$ in the case of a cylinder whose length is eight times the radius are given below for various values of the emissivity.

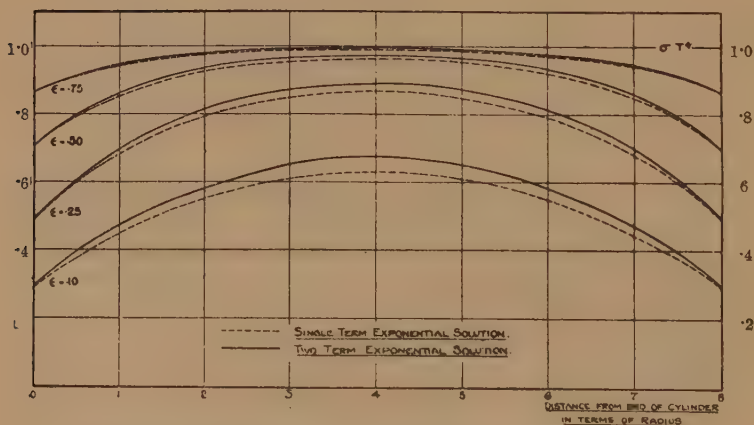
$$\epsilon = 0.75. \Phi(x) = 1 - 0.1399 e^{-0.980x} - 0.1399 e^{-0.980(8-x)} \\ + 0.0059 e^{-3.425x} + 0.0059 e^{-3.425(8-x)},$$

$$\epsilon = 0.50. \Phi(x) = 1 - 0.3011 e^{-0.795x} - 0.3011 e^{-0.795(8-x)} \\ + 0.0089 e^{-3.450x} + 0.0089 e^{-3.450(8-x)},$$

$$\epsilon = 0.25. \Phi(x) = 1 - 0.5064 e^{-0.558x} - 0.5064 e^{-0.558(8-x)} \\ + 0.0080 e^{-3.470x} + 0.0080 e^{-3.470(8-x)},$$

$$\epsilon = 0.10. \Phi(x) = 1 - 0.6680 e^{-0.352x} - 0.6680 e^{-0.352(8-x)} \\ + 0.0055 e^{-3.470x} + 0.0080 e^{-3.470(8-x)}.$$

Fig. 1.



Distribution of radiation from the inside of a uniformly heated finite cylinder.

The approximate solution for $n=1$ is given by

$$\Phi(x) = 1 - \frac{(1-\epsilon) \{e^{-\sqrt{\epsilon}x} + e^{-\sqrt{\epsilon}(l-x)}\}}{(1+\sqrt{\epsilon}) + (1-\sqrt{\epsilon})e^{-\sqrt{\epsilon}l}},$$

which, when $l \rightarrow \infty$ becomes

$$\Phi(x) = 1 - (1-\sqrt{\epsilon})e^{-\sqrt{\epsilon}x},$$

and agrees with the value obtained previously.

These results are shown graphically in fig. 1. As before, the agreement between the two approximate solutions is quite good for values of ϵ greater than 0.25. It is to be anticipated that the solution for a three-term exponential

approximation to $\frac{1}{2} \frac{d^2}{dx^2} F(x)$ will be very close to that given by the two-term exponential approximation for the reasons discussed in the previous paper.

*Circular Cylindrical Shaft or Light Well illuminated
by a Uniform Sky.*

Infinite Cylindrical Shaft.

The results obtained previously give the value of the radiation from any point x , of the infinite cylinder as

$$\Phi(x) = 1 + A_1 e^{a_1 x} + A_2 e^{a_2 x}$$

$$\text{or} \quad 1 - (1 - \sqrt{\epsilon}) e^{-\sqrt{\epsilon} x}.$$

If the end of the cylinder is closed by a circular disk of emissivity unity, and consequently of reflectivity zero, at the same temperature as the walls of the cylinder, the cylinder will approach the thermo-dynamic ideal of a constant temperature enclosure. Hence the radiation from every point on the walls of the cylinder is complete or black-body radiation. Thus, if $\theta(x)$ is the radiation from any point x in the cylinder when the end disk is in position, $\theta(x) = 1$.

Now let $\theta(x) - \Phi(x) = \Psi(x)$.

But $\theta(x) - \Phi(x)$ is merely the difference between what the walls radiate when the end disk is in position and what they radiate when it is not in position. What they radiate in each case is the radiation corresponding to the emissivity increased by multiple reflexion from the walls alone, since the disk at the end has zero reflectivity. Hence the difference $\Psi(x)$ is the radiation from the walls due to the radiation received by them from the end disk, increased by multiple reflexions from the walls.

$$\text{Hence} \quad \Psi(x) = -(A_1 e^{a_1 x} + A_2 e^{a_2 x})$$

$$\text{or} \quad (1 - \sqrt{\epsilon}) e^{-\sqrt{\epsilon} x}.$$

The same result is obtained if the end disk is replaced by an infinite disk having the same properties as the end disk but removed to an infinite distance. It also holds if the cylinder is not self-radiating, since what the walls radiate due to the presence of the disk is independent of what they radiate on their own account.

If, now, the infinite disk of unit emissivity be replaced by a uniform sky of brightness B , the sky can be regarded as

having zero reflectivity, so that the same result still applies if σT^4 is replaced by πB , and the reflectivity of the cylinder ($1 - \epsilon$) replaced by ρ . Hence the radiation from the cylinder when illuminated by a uniform sky of brightness B , i. e. the brightness of the walls of the infinite cylinder, is given by

$$\Psi_B(x) = -\pi B (A_1 e^{\alpha_1 x} + A_2 e^{\alpha_2 x})$$

or $\pi B (1 - \sqrt{1 - \rho}) e^{-\sqrt{1 - \rho} x}.$

Finite Cylindrical Shaft.

The similar problem for a finite cylinder does not submit to such general treatment as is given above, and resort must be made to calculation.

The radiation directly received by a disk of radius r at a distance x from a radiating disk at the end of a cylinder of radius r is given by

$$\frac{\pi E}{2} \{x^2 + 2r^2 - x(x^2 + 4r^2)^{\frac{1}{2}}\}$$

or $\frac{\pi E}{2} \{x^2 + 2 - x(x^2 + 4)^{\frac{1}{2}}\},$

where E is the radiation emitted per unit area of the radiating disk and x is expressed in terms of r .

Hence the radiation received per unit area by an elementary annulus of width dx at x is given by

$$-\frac{E}{4} \frac{d}{dx} \{x^2 + 2 - x(x^2 + 4)^{\frac{1}{2}}\} = -\frac{E}{4} \frac{d}{dx} F(x),$$

but $\frac{1}{2} \frac{d^2}{dx^2} F(x) = e^{-x}$ or $\{B_1 e^{\beta_1 x} + B_2 e^{\beta_2 x}\};$

$$\therefore -\frac{1}{2} \frac{d}{dx} F(x) = e^{-x} \text{ or } \left\{ \frac{B_1}{\beta_1} e^{\beta_1 x} + \frac{B_2}{\beta_2} e^{\beta_2 x} \right\}.$$

Consider, now, a finite cylinder of length l , emissivity ϵ , closed at one end by a disk of emissivity unity, both disk and cylinder being at the same temperature. Then the radiation emitted at any point x on the cylinder is the radiation directly emitted, together with the reflected portion of the radiation received from the disk and from the rest of the cylinder.

$$\therefore \theta(x_1) = \epsilon - \frac{1-\epsilon}{4} \frac{d}{dx} F(x) \\ + \frac{1-\epsilon}{4} \left\{ \int_0^{x_1} \theta(x) \frac{d^2}{dx^2} F(x_1-x) dx \right. \\ \left. + \int_{x_1}^l \theta(x) \frac{d^2}{dx^2} F(x-x_1) dx \right\}.$$

For the single-term exponential approximation the equation becomes

$$\theta(x_1) = \epsilon + \frac{1-\epsilon}{2} e^{-x} + \frac{1-\epsilon}{2} \left\{ \int_0^{x_1} \theta(x) e^{-(x_1-x)} dx \right. \\ \left. + \int_{x_1}^l \theta(x) e^{-(x-x_1)} dx \right\}.$$

Assuming that

$$\theta(x) = A_0 + A_1 e^{a_1 x} + A_1' e^{a_1(l-x)}$$

after substituting in the equation, performing the integrations, and equating on each side of the equation the constant terms and the coefficients of $e^{a_1 x_1}$, $e^{a_1(l-x_1)}$, e^{-x_1} , and $e^{-(l-x_1)}$ respectively, it is found that

$$\theta(x) = 1 + \frac{(1-\epsilon) \{ (1-\sqrt{\epsilon}) e^{-\sqrt{\epsilon}(l+x)} - (1+\sqrt{\epsilon}) e^{-\sqrt{\epsilon}(l-x)} \}}{(1+\sqrt{\epsilon})^2 - (1-\sqrt{\epsilon})^2 e^{-2\sqrt{\epsilon}l}},$$

which, when $l \rightarrow \infty$, gives $\theta(x) = 1$ as before.

But for the finite cylinder without the end disk,

$$\Phi(x) = 1 - \frac{(1-\epsilon) \{ e^{-\sqrt{\epsilon}x} + e^{-\sqrt{\epsilon}(l-x)} \}}{(1+\sqrt{\epsilon}) + (1-\sqrt{\epsilon}) e^{-\sqrt{\epsilon}l}};$$

$$\therefore \Psi(x) = \theta(x) - \Phi(x)$$

$$= \frac{(1-\epsilon) \{ (1+\sqrt{\epsilon}) e^{-\sqrt{\epsilon}x} - (1-\sqrt{\epsilon}) e^{-\sqrt{\epsilon}(2l-x)} \}}{(1+\sqrt{\epsilon})^2 - (1-\sqrt{\epsilon})^2 e^{-2\sqrt{\epsilon}l}},$$

which, when $l \rightarrow \infty$, gives

$$\Psi(x) = (1-\sqrt{\epsilon}) e^{-\sqrt{\epsilon}x}, \text{ as before.}$$

Thus the brightness of the walls of the finite cylinder when illuminated by a uniform sky of brightness B at one end is given by

$$\Psi_B(x) = \frac{\pi B \rho \{ (1+\sqrt{1-\rho}) e^{-\sqrt{1-\rho}x} - (1-\sqrt{1-\rho}) e^{-\sqrt{1-\rho}(2l-x)} \}}{(1+\sqrt{1-\rho})^2 - (1-\sqrt{1-\rho})^2 e^{-2\sqrt{1-\rho}l}}.$$

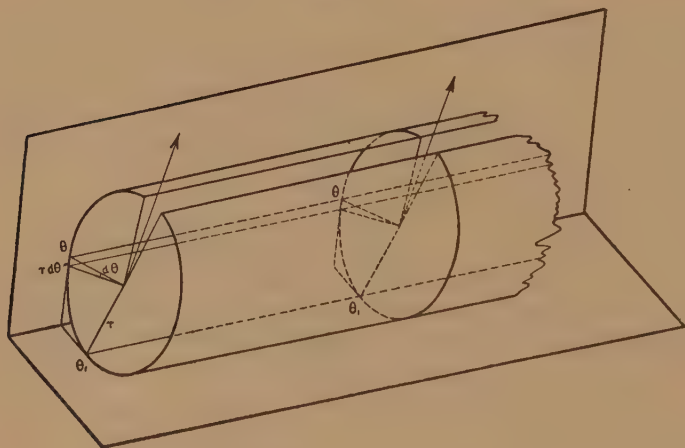
For the two-term exponential approximation the solution can be found by assuming that

$$\theta(x) = A_0 + A_1 e^{\alpha_1 x} + A_1' e^{\alpha_1(l-x)} + A_2 e^{\alpha_2 x} + A_2' e^{\alpha_2(l-x)},$$

and proceeding as before.

It should be noted that the approximate solutions obtained when the cylinder is not self-radiating are not as accurate as those obtained when the cylinder itself is radiating, since the former problem is solved by taking the difference between two solutions, of which at least one is an approximation. When the difference becomes small it may be considerably in error.

Fig. 2.



The Infinite Circular Cylinder with an Infinite Longitudinal Slit.

Consider an infinite cylinder with an infinite longitudinal slit parallel to the axis of the cylinder, subtending an angle 2ω at the axis as in fig. 2. It is obvious that the radiation emitted will be the same for all points on an elementary strip parallel to the longitudinal slit.

Let the origin of angular coordinates be taken as the line bisecting the slit. Then the radiation received per unit area at θ_1 from an infinite strip of width $r d\theta$ at θ is the same as the radiation from an infinite strip of width $r d\theta$ in the tangent plane at θ to the point θ_1 in the tangent plane at θ_1 .

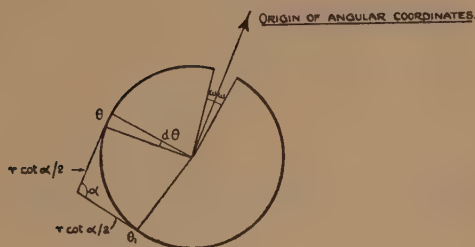
Now, α is the angle between the tangent planes at θ and θ_1 , so that it equals $\pi - (\theta_1 - \theta)$, while θ and θ_1 are situated at a distance $r \cot \alpha/2$ from the intersection of the two planes as shown in fig. 3.

The radiation to θ_1 from the area $r d\theta dy$ in the strip θ at a distance y from the plane normal to the axis of the cylinder and in which the receiving point θ_1 is situated is given per unit area by

$$\frac{\Phi(\theta) r d\theta dy}{\pi (4r^2 \cos^2 \alpha/2 + y^2)} \cdot \frac{r^2 \cot^2 \alpha/2 \cdot \sin^2 \alpha}{(4r^2 \cos^2 \alpha/2 + y^2)},$$

where $\Phi(\theta)$ is the total radiation per unit area from the

Fig. 3.



elementary strip at θ . The radiation from the infinite strip is therefore

$$\frac{\Phi(\theta)}{\pi} r^3 \cot^3 \alpha/2 \cdot \sin^2 \alpha d\theta \int_{-\infty}^{+\infty} \frac{dy}{(4r^2 \cos^2 \alpha/2 + y^2)}.$$

On putting $y = 2r \cos \alpha/2 \cdot \tan \beta$, this reduces to

$$\frac{\Phi(\theta)}{4} \cos \frac{\alpha}{2} d\theta = \frac{\Phi(\theta)}{4} \sin \frac{\theta_1 - \theta}{2} d\theta.$$

Hence the integral equation giving the required solution is

$$\Phi(\theta_1) = \epsilon + \frac{1 - \epsilon}{4} \left\{ \int_{\omega}^{\theta'} \Phi(\theta) \sin \frac{\theta_1 - \theta}{2} d\theta + \int_{\theta'}^{2\pi - \omega} \Phi(\theta) \sin \frac{\theta - \theta_1}{2} d\theta \right\}.$$

On differentiating twice with respect to θ_1 , it is found that

$$4\Phi''(\theta_1) = \epsilon - \epsilon\Phi(\theta_1),$$

so that

$$\Phi(\theta_1) = 1 + A \cos \frac{\sqrt{\epsilon}\theta_1}{2} + B \sin \frac{\sqrt{\epsilon}\theta_1}{2},$$

where A and B are undetermined constants. But from considerations of symmetry

$$\Phi(\theta) = \Phi(2\pi - \theta).$$

Hence

$$B = A \tan \sqrt{\epsilon}\pi/2.$$

Since the integral equation holds for all values of θ' ; $\omega < \theta' < 2\pi - \omega$ it holds for $\theta_1 = \pi$, so that

$$1 + A \cos \sqrt{\epsilon}\pi/2 + B \sin \sqrt{\epsilon}\pi/2 = \epsilon + \frac{1-\epsilon}{2}$$

$$\int_{\omega}^{\pi} (1 + A \cos \sqrt{\epsilon}\theta/2 + B \sin \sqrt{\epsilon}\theta/2) \cdot \cos \theta/2 \cdot d\theta.$$

On integrating this equation and putting

$$B = A \tan \sqrt{\epsilon}\pi/2,$$

it follows that

$$A = \frac{-(1-\epsilon) \sin \omega/2 \cdot \cos \sqrt{\epsilon}\pi/2}{\sqrt{\epsilon} \cos \omega/2 \cdot \sin \sqrt{\epsilon}(\pi-\omega)/2 + \sin \omega/2 \cdot \cos \sqrt{\epsilon}(\pi-\omega)/2}$$

and

$$B = \frac{-(1-\epsilon) \sin \omega/2 \cdot \sin \sqrt{\epsilon}\pi/2}{\sqrt{\epsilon} \cos \omega/2 \cdot \sin \sqrt{\epsilon}(\pi-\omega)/2 + \sin \omega/2 \cdot \cos \sqrt{\epsilon}(\pi-\omega)/2}.$$

Hence

$$\Phi(\theta) = 1 - \frac{(1-\epsilon) \sin \omega/2 \cdot \cos \sqrt{\epsilon}(\pi-\theta)/2}{\sqrt{\epsilon} \cos \omega/2 \cdot \sin \sqrt{\epsilon}(\pi-\omega)/2 + \sin \omega/2 \cdot \cos \sqrt{\epsilon}(\pi-\omega)/2};$$

i. e.,

$$\Phi(\theta) = 1 - C \cos \sqrt{\epsilon}(\pi-\theta)/2,$$

where

$$C = \frac{(1-\epsilon) \sin \omega/2}{\sqrt{\epsilon} \cos \omega/2 \cdot \sin \sqrt{\epsilon}(\pi-\omega)/2 + \sin \omega/2 \cdot \cos \sqrt{\epsilon}(\pi-\omega)/2}.$$

Now,

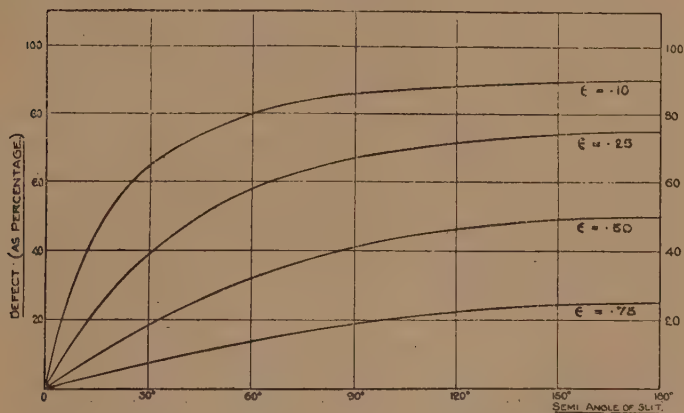
$$C \cos \sqrt{\epsilon}(\pi-\theta)/2$$

is the "defect" from black-body radiation as a function of θ and of ω , the semi-angle of the slit. This is shown graphically in fig. 4 for values of the emissivity of 0.10, 0.25, 0.50, and 0.75 for $\theta = \pi$, *i. e.*, positions directly opposite the centre of the slit.

The solution of the inverse problem of the brightness of a similar cylinder of reflectivity ρ , illuminated by a uniform sky of brightness B , is easily obtained as

$$\Psi_B(\theta) = \frac{\pi B \rho \sin \omega/2 \cdot \cos \sqrt{1-\rho}(\pi-\theta)/2}{\sqrt{1-\rho} \cos \omega/2 \cdot \sin \sqrt{1-\rho}(\pi-\omega)/2 + \sin \omega/2 \cdot \cos \sqrt{1-\rho}(\pi-\omega)/2}.$$

Fig. 4.



Defect of black-body radiation opposite slit in infinite cylinder.

Summary.

The paper is a continuation of a previous one in which the effect of multiple reflexion from the walls of a uniformly-heated infinite cylinder in building up black-body radiation is considered. The method is now applied to the case of a finite uniformly-heated cylinder, and an approximate solution is obtained. The results are of interest in showing how closely a uniformly-heated cylinder can approach the ideal black-body radiator.

It is also shown how the brightness of the inside of a non-radiating cylinder illuminated by a uniform sky can be deduced from the solution of the problem of the self-radiating cylinder. This is the case of a light well.

The problem of the radiation from the inside of a uniformly-heated infinite cylinder having an infinite longitudinal slit is also solved. In this case the solution of the integral equation is exact. The results are of interest in showing how closely a radiator of the type of Ives's primary standard of light approaches the ideal black-body radiator.

XLVI. *A Quartz Fibre Electrometer.* By D. R. BARBER,
*B.Sc., A.Inst.P., Research Student, Department of Physics,
 University College of the South-West of England, Exeter* *.

1. Introduction.

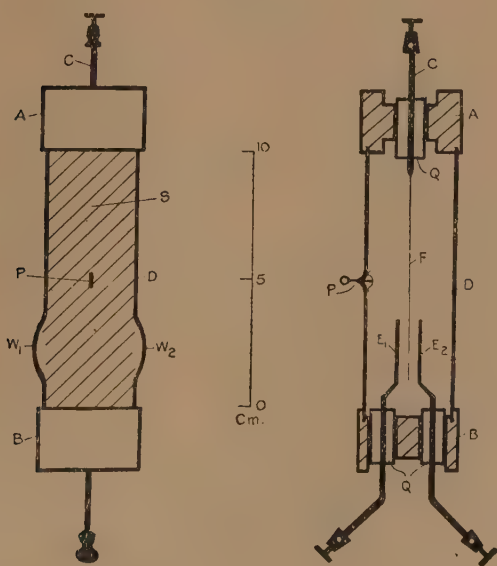
THE quantity of electricity which escapes from a charged body is very small, and it is necessary that the capacity of the instrument used to measure it should be small. This condition makes it advisable to use a small gold-leaf electroscope. It has been found that the gold leaf may be replaced by a single fibre of quartz, rendered conductive by the deposition of a suitable metallic film. In preliminary experiments the fibres employed, approximately 1 mil (2.5×10^{-2} mm.) diameter, were silvered by chemical deposition. This method ultimately proved unsatisfactory, the films becoming discontinuous a short time after their formation. Cathode disintegration of the metal "*in vacuo*" was finally adopted, and the "sputtered" fibres obtained by this method have proved very satisfactory. At first the electric field was applied between a single insulated plate and the containing case, the vertically suspended fibre being illuminated laterally and viewed through a microscope against a dark background. An "earthed" metal cylinder provided with windows formed the case of the instrument. It was found, however, that this type of electrometer suffered from two serious defects: (a) an erratic displacement of the fibre, which was independent of the electrical condition of the instrument, and was eventually traced to thermal radiations from the light-source, incident upon the fibre, causing the metal film and the quartz to dilate by unequal amounts. This effect was apparent even when reflected sunlight was used as the illuminant; (b) there was a non-linear relation between the P.D. applied to the fibre, and the resultant deflexion, except for very small field values. Under these conditions it would thus be necessary to calibrate the instrument over the entire working range. The design of the electroscope was therefore modified by using two parallel plates and direct illumination, *i. e.* the fibre was viewed against a bright background. The latter method, since it requires only a fraction of the illumination necessary in the former, does not give rise to any extraneous thermal effects.

* Communicated by Prof. F. H. Newman, D.Sc., F.Inst.P.

2. Description of the Instrument.

The instrument in its final form is shown diagrammatically in fig. 1. A silvered quartz fibre F is attached to a copper electrode C by a small globule of Wood's metal, and hangs symmetrically between the two electrodes, E_1 and E_2 , of sheet brass 2.5×2.0 cm. and separated by an air-gap 7.5 mm. wide. The leads from the plates pass through short lengths of quartz tube Q , cemented into the lower ebonite cap B and the fibre electrode is similarly insulated

Fig. 1.



by the quartz sleeve Q , cemented into the upper ebonite cap A . The case of the instrument is a glass tube D , 10.0 cm. long by 3.5 cm. diameter, provided with two windows W_1 and W_2 , slightly blown out in order to free the glass of air-bubbles, and, with the exception of the windows, it is coated on the inside with a film of silver, S . Contact with this is made by the platinum wire P , sealed through the glass, and terminating on the exterior in a loop electrode by means of which the silver coating is connected to earth. The ebonite cups were grooved concentrically to fit closely on to the cylindrical glass case, this method of assembly enabling the instrument to be easily dismantled, if the necessity arose

for subsequent modification in the relative position of fibre and plates.

Some trouble was experienced, initially, in mounting the fibre preparatory to the sputtering process, but after several ineffective trials, the following technique was adopted. The selected fibre was stretched across a rectangular glass frame, its two ends being cemented by means of shellac, and the frame was then held horizontally in a clamp, care being taken that the fibre was quite clear of the clamp edges. The electrode serving as the fibre support consisted of a straight copper wire, flattened at one extremity, and in this a fine groove was cut to receive the fibre. The wire was first fitted into its insulating sleeve and cap, and the tip was then "tinned" with Wood's metal, care being taken that the groove was completely filled with the metal. This tinned portion was then bent through an angle of about 20° , and the assembly clamped vertically beneath the fibre frame, in such a position that the wire was just in contact with, and parallel to, the fibre. A well-heated soldering-iron was placed against the under side of the wire, and the Wood's metal melted, a slight downward pressure being applied to the stretched fibre meanwhile, so that it sunk into its groove, this pressure being maintained until the molten metal solidified. The wire was finally straightened and the fibre cut to the requisite length, a fragment of glass being attached to its extremity to keep it taut when placed in the discharge-tube.

The discharge apparatus used for the cathode deposition of silver upon the fibre consisted of a vertical tube in which the fibre was suspended. Sealed to this was a horizontal side tube which served to connect the main tube to the exhaust system. The cathode of 60-mesh pure silver gauze formed a vertical cylindrical tube, concentric with, and entirely enclosing, the fibre and the "tinned" end of the copper electrode. A cup-shaped electrode of brass supported the cathode. The fibre having been lowered into position, its ebonite supporting cap was sealed down with wax and the tube evacuated. A 10 inch induction coil with a mechanical interrupter was used to excite the tube, and a continuous discharge was maintained for 30 minutes. Care was taken to protect the under surface of the insulating cap so as to prevent the possible formation of a silver deposit upon the ebonite surface. "Sputtering" of the silver readily occurred at a pressure of 5.0×10^{-3} mm. of mercury, and this pressure, after a sudden initial rise, remained constant throughout the period of discharge.

Fibres treated in this way were coated with a very uniform and coherent layer of metal, and a satisfactory electrical connexion between the fibre coating and the support was obtained. This is extremely important, since it was always at the junction of fibre and support that the chemically deposited layer, used in the earlier experiments, became discontinuous. Fibres coated by cathode disintegration showed practically no increase in diameter when examined under the microscope, and although no direct measurements have been made, it is estimated that these metallic films have an actual thickness of the order of 10^{-5} mm.

3. Calibration of the Instrument.

The instrument was calibrated directly by applying known P.D.'s to the fibre, with a constant field maintained between the two fixed electrodes.

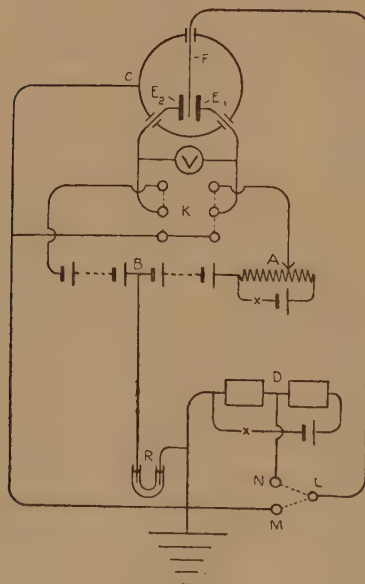
Measurements of the resultant deflexions were made by observations of the fibre image in the field of a telemicroscope, 25 divisions of the eyepiece scale corresponding to an actual displacement of 1.0 mm. Readings were taken, for a particular field value, corresponding to increasing fibre potentials over the range (0.0–2.1 volts), and these were repeated at measured plate voltages between 35 and 60 volts.

The circuit used for this calibration is shown in fig. 2. The two plates E_1 and E_2 of the electrometer are joined, through the double pole switch K, to the positive and negative terminals of a 60-volt H.T. battery B, whose centre tapping is "earthed." The switch K is included in order that a P.D. may be applied to the plates simultaneously, as attempts to excite them separately invariably result in the fibre flying across the field and sticking to the plate. A commutator of the mercury contact type with its inter-connecting copper strips removed forms a convenient arrangement, and by using the two additional cups the electrometer plates may be "earthed" when no potential is applied to them. The adjustment is useful when obtaining the zero position of the fibre.

With the double-plate type of electrometer it is essential that the relative positions of fibre and electrodes remain unaltered whenever the electric field is applied, since any displacement which occurs entails re-calibration of the instrument. A potentiometer A joined in series with the battery B provides the necessary fine adjustment whereby the fibre may be restored to its zero position. This adjustment is made whenever the field is switched on previous to

making a series of observations. A voltmeter V is joined across the electrode leads, and measures the applied plate P.D. Varying potentials are applied to the fibre F by means of the potential divider D . Connexion from this to the fibre conductor is made by means of the mercury cups L , M , and N in a block of paraffin wax. When L and M are joined by means of an insulated "bridge" of copper wire, the fibre is "earthed." On breaking this circuit and joining L and N , connexion is made with D , and the fibre is raised to the required potential. The case C of

Fig. 2.



the instrument is "earthed," and a water resistance R is joined in series with the earth lead from the centre tapping of B , so that, in the event of the "earthed" fibre touching either of the plates, no short-circuit can occur.

4. Experimental Results.

The results obtained with the instrument were very consistent, and, as was anticipated, the relation between the potential applied to the fibre and the resultant displacement was found to be linear within the limits of experimental error.

The displacement period of the fibre was found to be comparatively short, the deflexion being complete in approximately 5 secs.

The results of the calibration are shown in fig. 3, and the sensitivity at different potential differences applied to the plates is given in Table I.

Fig. 3.

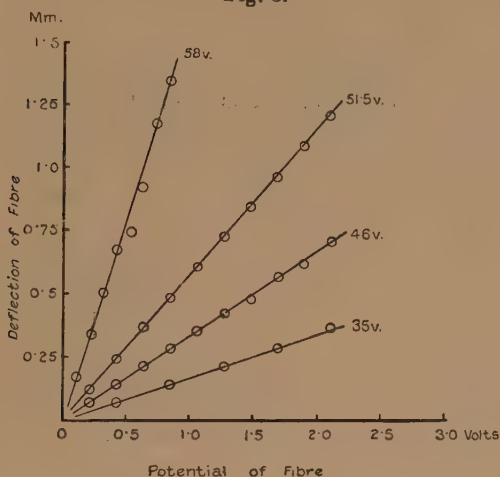


TABLE I.

P.D. applied to plates (volts).	P.D. range applied to fibre (volts).	Deflexion of fibre (mm.).	Sensitivity mm./volt.
35.0	0.42 -2.10	0.07-0.36	0.168
46.0	0.21 -2.10	0.07-0.70	0.330
52.0	0.21 -2.10	0.12-1.20	0.570
58.0	0.105-0.84	0.17-1.34	1.560
59.5	0.021-0.168	0.05-0.47	2.600

From the curves it will be seen that there is a linear relation between the potential applied to the fibre and the deflexion over the entire range of plate potential, viz. 36 to 60 volts.

At 58 volts, however, the calibration range becomes restricted, the fibre being unstable with an applied potential

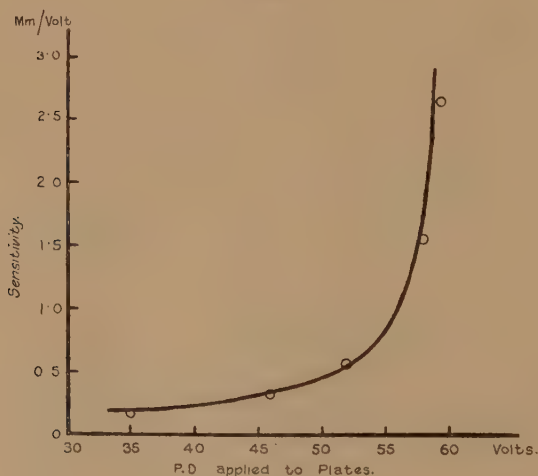
of 0.95 volt. This points to a critical value in the neighbourhood of 60 volts for the plate potential of the instrument described, and this result has been confirmed by interpolation, using the empirical relation found to exist between plate potential and mean sensitivity.

The capacity of the instrument, as measured by sharing its charge with a quadrant electrometer, was found to be approximately 3 cm.

5. Sensitivity of the Instrument.

Sensitivity has been defined as the actual displacement, in millimetres of the fibre, per unit potential applied to it

Fig. 4.



This has been adopted, since it makes direct comparison possible with the values found for other instruments. Using the above definition, we can express the relation between sensitivity S and plate potential V by the equation

$$S(V-61) = \div 4.9.$$

This curve is reproduced in fig. 4. Putting $S = \infty$ in the above, we obtain a value of 61 volts for the critical plate potential difference, *i. e.* the potential at which the fibre becomes unstable.

It is interesting to compare the sensitivity values with those quoted for other electrometers of varying types.

Kaye*, using a modified form of Wilson's tilted leaf electroscope, obtained a sensitivity of 5.5 mm./volt over the range 0.8–1.20 volt, with a plate P.D. of 207 volts.

Using a double-plate electrometer in which a quartz fibre 0.003 mm. diameter was anchored at either end, Laby† found that with a plate P.D. of 60 volts, the plates being 1 cm. apart, 1 volt applied to the fibre gave a deflexion of 0.2 mm. As would be expected with a stretched fibre, this value of S is lower than that observed by the author, using the suspended fibre instrument. More recently Lindemann and Keeley‡ have devised a torsional quartz-fibre electrometer in which two silvered needles, capable of rotation about a horizontal axis, are mounted perpendicularly to the torsion fibre. These needles move in an electric field between two pairs of fixed plates, and their movement is constrained by the torsion of the suspended fibre. With a fibre 6μ diameter and 1.4 cm. long, the attached needles being 17μ diameter and 0.9 cm. long, a sensitivity of .76 mm./volt was obtained with a plate P.D. of 97 volts, the plate separation being 0.6 cm.

The high sensitivity obtained at comparatively low plate potentials, and the stability of the fibre over extended periods of observation, are advantages claimed for the present instrument.

6 Summary.

1. A description is given of a double-plate electrometer employing a single suspended quartz fibre as the moving system.

2. A method of rendering the quartz conducting by cathode disintegration of silver is given, with a description of the technique developed in handling and mounting the fibres.

3. The results of a direct calibration of the instrument are given, and compared with those obtained by other investigators using different types of electrometers.

In conclusion, the author wishes to thank Prof. F. H. Newman, D.Sc., and Mr. V. H. L. Searle, M.Sc., for their kindly interest and helpful suggestions throughout the course of this investigation.

* Kaye, G. W. C., Proc. Phys. Soc. vol. xxiii. pp. 209–218 (1911).

† Laby, T. H., Proc. Camb. Phil. Soc. vol. xv. pp. 106–113 (1909).

‡ Lindemann, F. A., and Keeley, T. C., Phil. Mag. vol. xlvii. pp. 577–583 (1924).

XLVII. *New Bands in the Secondary Spectrum of Hydrogen.*

By D. B. DEODHAR, *M.Sc., Ph.D., Physics Research Laboratory, King's College, London**.

IN the present paper it is proposed to deal with seven new bands in the secondary spectrum of hydrogen situated in the yellow region.

An attempt at suggesting possible groups of related lines in the yellow region was made by Kimura and Nakamura † by studying the electrodeless discharge of hydrogen, and recently Curtis ‡ grouped some prominent lines in that region under the heading of K, G, and H series. As to the relevance of the H group, Curtis himself appears to be uncertain. Curtis's K group consists of seven lines and the G group six lines. The second differences of the G's are rather irregular, though the second differences of the K's are good. Again, there is no relationship between the three groups.

It is now well known that the study of the spectrum of hydrogen under the conditions of excitation known as the first-type discharge lends a great help in picking out related lines on account of their selective enhancement or weakening of intensities in such a discharge. A study of the microphotograph of the first-type spectrum plate taken by Moll's self-registering photometer was made by the present author, at King's College, during the investigation on Fulcher systems, and it was seen that, in addition to the Fulcher group recently analysed by Prof. O. W. Richardson, the microphotograph possessed another distinct group situated in the yellow region. It appeared from the microphotograph that Curtis's K and G series were components of a system of seven bands. The bands are such that the successive corresponding lines in Curtis's K and G groups stand as P(2)'s and P(3)'s in each of the seven bands. Curtis's G group contains only six members. To these I have added 17729.30 (*q*) as the relevant seventh member. This line was picked up from the microphotograph, and it fits in as P(3) of the seventh band. Some Q branches were picked from the microphotograph, while the rest of the Q branches and R branches were developed by examining the behaviour of "condenser-discharge" lines in the first-type spectrum.

* Communicated by Prof. O. W. Richardson, D.Sc., F.R.S.

† Japan Journ. Phys. i. p. 86 (1923).

‡ Phil. Mag. i. p. 695 (1926).

The bands are named as D_1 , D_2 , D_3 , D_4 , D_5 , D_6 , and D_7 , and their properties and other details are given in Table I. The horizontal and vertical difference are given in Tables II. and III. respectively. In Table I. the band lines are represented by their wave-numbers, followed by (1) the intensity estimates given in the tables of Merton and Barratt*, Tanaka†, or Deodhar‡, and (2) the intensity estimate on the first-type plate. The lines from Tanaka's and Deodhar's tables are marked by the letters T or D underneath. The other letters denote the properties of the lines as given in Merton and Barratt's tables, with the notation H.P.=high pressure, L.P.=low pressure, C.D.=condensed discharge, He=Helium effect, Z=Zeeman effect, and S=Stark effect. These are followed by claims made by other systems. The first and second differences are given in the next two columns.

The line $D_2 P(3)$ figures as Richardson's § 157 Q(4), but it is an unresolved doublet according to Merton and Barratt's tables. $D_3 P(3)$ is claimed as 186 R(2) ||, but its intensity appears to be rather uncertain there. $D_4 P(2)$ coincides with 201 R(2) ¶, but its intensity seems to be too great as a member of 201 R(m). Similarly, $D_6 P(2)$ appears to be rather too strong to fit well in Richardson and Tanaka's series 81 R(m)**. It may be pointed out that Richardson and Tanaka think 81 R(7) to be double. The line $D_2 Q(2)$ coincides with $D_3 Q(5)$ and with Richardson's 156 Q(m); but the fact that it is extremely weakened in the first-type discharge favours its claim as $D_2 Q(2)$ and $D_3 Q(5)$ as well. $D_2 Q(3)$ looks abnormal in intensity. However, its condensed discharge nature may favour its position there. $D_2 Q(5)$ is also claimed as 156 Q(5) and 159 R(8) ††; Richardson thinks that the strength of the line can allow it to be a member of two series, and owing to its weakening in the first-type discharge, it seems reasonable that the line may have its place as $D_2 Q(5)$ as well. 17812.35 figures as $D_6 Q(4)$ and $D_4 R(4)$. Its position as $D_6 Q(4)$ appears to be more justifiable than its position as $D_4 R(4)$. However, as this line is not claimed by more series, its assignment as $D_4 R(4)$ may be retained for the present. The intensity of this line perhaps favours its

* Phil. Trans. A, ccxxii. pp. 369-400.

† Roy. Soc. Proc. A, cviii. pp. 593-606 (1925).

‡ *Ibid.* cxiii. pp. 420-432 (1926).

§ Proc. Roy. Soc. A, cix. p. 240 (1925).

|| *Ibid.* p. 249 (1925).

¶ Proc. Roy. Soc. A, cvi. p. 663 (1924).

** *Ibid.* cvii. p. 617 (1925).

†† *Ibid.* cix. p. 246 (1925).

TABLE I.

$D_1 P(m)$		$D_1 Q(m)$		$D_1 R(m)$	
<i>m.</i>		<i>m.</i>		<i>m.</i>	
1.	16980.87 (o) (o) H.P.+, He+	1.	17139.43 (5) (1) C.D.++	1.	17266.83 (1) (ab) 5 L4, Q(3)
2.	16931.52 (o) (o) H.P.+, C.D.+, He+	2.	17108.44 (o) (1)	2.	17296.10 (1) (ab)
3.	16734.15 (5) (<o) H.P.+, C.D.+, He+	3.	17088.60 (2) (<o) C.D.++, H.E.++	3.	17318.72 (o) (ab) He++
4.	16730.52 (o) (ab)	4.	17013.55 (1) (ab) C.D.+	4.	17325.23 (qd) (ab)
5.		5.	16943.09 (1) (<o) C.D.+, He+		
$D_2 P(m)$		$D_2 Q(m)$		$D_2 R(m)$	
<i>m.</i>		<i>m.</i>		<i>m.</i>	
1.	17130.36 (9) (6) L.P.++, C.D.++	1.	17266.83 (1) (ab) D ₁ R(1)	1.	17375.80 (o) (ab)
2.	17025.82 (4) (4) L.P.++, C.D.++, 157 Q(4)	2.	17239.74 (3) (ab) C.D.++, 156 Q(5)	2.	17416.54 (2) (ab) C.D.+
3.	16906.94 (q) (ab) T	3.	17202.55 (3) (4) C.D.++, He++	3.	17446.38 (o) (ab)
4.	16774.72 (8) (4) H.P.+, C.D.+, He+, Z	4.	17151.52 (-) (ab) He+++, 201 R(q)	4.	17463.80 (q) (ab) T
5.		5.	17086.69 (2) (1) 156 Q(6), 159 R(8)		

$D_3 P(m).$

<i>m.</i>	
2.	17278.89 (7) (7) L.P. + +, C.D. +
3.	17169.12 (5) (6) L.P. + +, C.D. + +, 186 R(2)
4.	17047.13 (5) (1) H.P. + +, C.D. + +
5.	16915.38 (2) (1)

$D_3 Q(m).$

<i>m.</i>	
1.	17407.53 (o) (ab) 171 P(2)
2.	17383.08 (q) (ab) He +
3.	17348.19 (2) (ab) C.D. + +
4.	17299.42 () (o) H.P. + +, C.D. + +, He + +
5.	17289.74 (3) (ab) C.D. + +, He +, 156 q(5), D ₂ Q(2)

$D_4 P(m).$

<i>m.</i>	
2.	17426.25 (8) (6) C.D. +, 201 R(2)
3.	17311.28 (7) (6) L.P. + +, C.D. + +
4.	17184.43 (1) (2) C.D. + +
5.	17051.84 (v) (ab) D

$D_4 Q(m).$

<i>m.</i>	
1.	17557.13 (2) (o)
2.	17533.13 (rad) (ab) D
3.	17501.57 (o) (prob. ab)
4.	17458.78 (1) (ab)
5.	17404.99 (o) (ab)

$D_3 R(m).$

<i>m.</i>	
1.	17512.36 (o) (prob. ab)
2.	17562.35 (o) (ab) O.D. + +, He + +
3.	17599.71 (rad) ² (ab) D
4.	17623.32 (1) (ab) C.D. + +, He + +

$D_4 R(m).$

<i>m.</i>	
1.	17664.50 (o) (ab) He + +
2.	17724.18 (q) (ab)
3.	17775.19 (1) (o)
4.	17812.35 (4) (1) C.D. +, D ₆ Q(4)

TABLE I. (continued).

$D_6 P(m).$	$D_6 Q(m).$	$D_6 R(m).$
$m.$ 1. 17572.31 (7) (4) C.D. + +, He + 2. 17451.61 (7) (4) H.P. +, C.D. + +, He +, 201 R(5) 3. 17018.72 (6) (ab) He + + 4. 17184.43 (1) (1) C.D. + +, 5 Q4, Q5	$m.$ 1. 17720.73 (rd) (ab) D 2. 17697.5 (-) (ab) T 3. 17664.50 (6) (ab) He + + 4. 17619.25 (-) (6) He + + 5. 17566.27 (2) (ab) C.D. +	$m.$ 1. 17846.91 (6) (ab) He -, 157 Q(7), 4 L3, R(3) 2. 17909.9 (-) (ab) T 3. 17966.00 (2) (6) C.D. + +, 83 Q(8) 4. 18000.57 (rd) (ab) D
$D_6 P(m).$	$D_6 Q(m).$	$D_6 R(m).$
$m.$ 1. 17716.87 (3) (1) O.D. + +, He +, 81 R(7) 2. 17591.33 (2) (6) C.D. + + 3. 17458.78 (1) (ab) O.D. + + 4. 17316.50 (3) (ab) C.D. + +	$m.$ 1. 17902.41 (-) (ab) He + + 2. 17879.71 (1) (6) C.D. + + 3. 17850.99 (3) (6) C.D. + +, He + + 4. 17812.35 (4) (1) D.P. + 5. 17765.11 (1) (6) C.D. + +, He + +	$m.$ 1. 18064.86 (6) (<6) C.D. + +, He + + 2. 18140.19 (-) (ab) He + + 3. 18305.52 (6) (ab) 4. 18260.14 (1) (1) L.P. +

[illegible]

allocation to more than one series. $D_5 R(3)$ is also given as $83 Q(8)^*$, but Richardson and Tanaka think it to be too strong for $83 Q(8)$.

The horizontal and vertical differences of $P(m)$, $Q(m)$, and $R(m)$ lines of all the bands are tabulated in Tables II. and III. It will be seen that the run of the horizontal differences in Table II. is fairly systematic except in one or two cases. The vertical differences assembled in Table III. show a very systematic variation for all the $P(m)$, $Q(m)$, and $R(m)$ lines of all bands.

TABLE II.

Horizontal Differences of $P(m)$'s, $Q(m)$'s, and $R(m)$'s.

$P(m)$.	$D_2 - D_1$.	$D_3 - D_2$.	$D_4 - D_3$.	$D_5 - D_4$.	$D_6 - D_5$.	$D_7 - D_6$.
$P(2)$	149.49	148.53	147.36	146.06	144.56	142.88
$P(3)$	144.30	143.30	142.16	140.33	139.72	137.97
$P(4)$	142.79	140.19	137.30	134.29	140.06	129.32
$P(5)$	144.20	140.66	136.46	132.59	132.07	119.75
$Q(1)$	127.40	140.70	149.60	163.60	181.68	205.53
$Q(2)$	131.30	143.34	150.05	164.37	182.21	207.10
$Q(3)$	133.95	145.64	153.38	162.93	186.49	207.53
$Q(4)$	137.97	147.90	159.36	160.47	193.10	208.37
$Q(5)$	143.60	153.05	165.25	161.28	198.84	210.19
$R(1)$	108.97	136.56	152.14	182.41	217.95	270.47
$R(2)$	120.44	145.81	161.83	185.72	230.29	277.00
$R(3)$	127.66	153.33	175.48	190.81	239.52	285.64
$R(4)$	138.57	159.52	189.03	188.22	259.57	298.79

TABLE III.

Vertical Differences of $P(m)$, $Q(m)$, and $R(m)$ lines.

	$P(2) - P(3)$.	$P(3) - P(4)$.	$P(4) - P(5)$.
D_1	99.35	117.37	133.63
D_2	104.54	118.88	133.22
D_3	109.77	121.99	131.75
D_4	114.97	126.85	132.59
D_5	120.70	132.89	134.29
D_6	125.24	132.55	142.28
D_7	130.45	141.20	151.85

* *Ibid.* cvii. p. 618 (1925).

TABLE III. (continued).

	Q(1)–Q(2).	Q(2)–Q(3).	Q(3)–Q(4).	Q(4)–Q(5).
D ₁	30.99	39.84	55.05	69.46
D ₂	27.09	37.19	51.03	64.83
D ₃	24.45	34.89	48.77	59.68
D ₄	24.00	31.56	42.79	53.79
D ₅	23.27	33.00	45.25	52.98
D ₆	22.70	28.72	38.64	47.24
D ₇	21.13	28.29	37.80	45.42

	R(2)–R(1).	R(3)–R(2).	R(4)–R(3).
D ₁	29.27	22.62	6.51
D ₂	40.74	29.84	17.50
D ₃	49.99	37.36	23.61
D ₄	59.68	51.01	37.16
D ₅	62.99	56.10	34.57
D ₆	75.33	65.33	54.62
D ₇	81.86	73.97	67.77

The P, Q, and R branches of all the bands obey the usual combination principle throughout, such as $Q(m+1) + Q(m) = P(m+1) + R(m)$. The accuracy with which the combination principle is obeyed shows the correctness of the associated branches; and the properties of the various lines and the manner in which the first differences vary from set to set appear to indicate that these seven bands are related to each other. This idea is further strengthened by looking to the systematic run of the ν_0 values from band to band and to the values of the moment of inertia assembled in Table VI.

Initial and Final Terms :—

We have, as usual,

$$R(m) = \nu_0 + F(m+1) - f(m), \quad \text{(i.) } (\overline{m+1} \rightarrow m)$$

$$Q(m) = \nu_0 + F(m) - f(m), \quad \text{(ii.) } (\overline{m} \rightarrow m)$$

$$\text{and } P(m) = \nu_0 + F(m-1) - f(m). \quad \text{(iii.) } (\overline{m-1} \rightarrow m)$$

In these equations ν_0 is the frequency of the origin of the band, and F and f stand for the initial and the final states respectively.

From these equations we see that

$$F(m+1) - F(m) = R(m) - Q(m) = Q(m+1) - P(m+1) \quad \text{(iv.)}$$

(Initial term difference)

and

$$f(m+1) - f(m) = R(m) - Q(m+1) = Q(m) - P(m+1). \quad \text{(v.)}$$

(Final term difference)

The initial and the final term differences of all the bands are tabulated in Tables IV. and V.

TABLE IV.

Initial Terms.

Band.	m .	$\frac{R(m)}{-Q(m)}$.	$\frac{Q(m+1)}{-P(m+1)}$.	Means.	Term diff.	2nd diff.
D_1	1 ...	127·40	127·57	127·48	$F(2) - F(1)$	$> 59·89$
	2 ...	187·66	187·08	187·37	$F(3) - F(2)$	$> 62·39$
	3 ...	250·12	249·40	249·76	$F(4) - F(3)$	$> 62·36$
	4 ...	311·68	312·57	312·12	$F(5) - F(4)$	
D_2	1 ...	108·97	109·38	109·17	$F(2) - F(1)$	$> 67·59$
	2 ...	176·80	176·73	176·76	$F(3) - F(2)$	$> 67·44$
	3 ...	243·83	244·58	244·20	$F(4) - F(3)$	$> 67·92$
	4 ...	312·28	311·97	312·12	$F(5) - F(4)$	
D_3	1 ...	104·83	104·19	104·51	$F(2) - F(1)$	$> 74·66$
	2 ...	179·27	179·07	179·17	$F(3) - F(2)$	$> 72·73$
	3 ...	251·52	252·29	251·90	$F(4) - F(3)$	$> 72·23$
	4 ...	323·90	324·36	324·13	$F(5) - F(4)$	
D_4	1 ...	107·37	106·88	107·125	$F(2) - F(1)$	$> 83·55$
	2 ...	191·05	190·29	190·67	$F(3) - F(2)$	$> 83·31$
	3 ...	273·62	274·35	273·98	$F(4) - F(3)$	$> 79·38$
	4 ...	353·57	353·15	353·36	$F(5) - F(4)$	
D_5	1 ...	126·18	125·19	125·68	$F(2) - F(1)$	$> 86·96$
	2 ...	212·4	212·89	212·64	$F(3) - F(2)$	$> 88·37$
	3 ...	301·50	300·53	301·01	$F(4) - F(3)$	$> 80·57$
	4 ...	381·12	381·84	381·58	$F(5) - F(4)$	
D_6	1 ...	162·45	162·84	162·64	$F(2) - F(1)$	$> 97·43$
	2 ...	260·48	259·66	260·07	$F(3) - F(2)$	$> 93·98$
	3 ...	354·53	353·57	354·05	$F(4) - F(3)$	$> 94·05$
	4 ...	447·79	448·61	448·20	$F(5) - F(4)$	
D_7	1 ...	227·39	227·06	227·22	$F(2) - F(1)$	$> 102·58$
	2 ...	330·38	329·22	329·80	$F(3) - F(2)$	$> 102·83$
	3 ...	432·64	432·62	432·63	$F(4) - F(3)$	$> 106·00$
	4 ...	538·21	539·05	538·63	$F(5) - F(4)$	

TABLE V.
Final Terms.

Band.	<i>m.</i>	$\frac{R(m)}{-Q(m+1)}.$	$\frac{Q(m)}{-P(m+1)}.$	Mean.	Term diff.	2nd diff.
D ₁	{ 1 ...	158·39	158·56	158·47	$f(2)-f(1)$	
	{ 2 ...	227·50	226·92	227·21	$f(3)-f(2)$	> 68·74
	{ 3 ...	305·17	304·45	304·81	$f(4)-f(3)$	> 77·60
	{ 4 ...	382·14	383·03	382·58	$f(5)-f(4)$	> 77·77
D ₂	{ 1 ...	136·06	136·47	136·26 ₅	$f(2)-f(1)$	
	{ 2 ...	213·99	213·92	213·95 ₅	$f(3)-f(2)$	> 77·69
	{ 3 ...	294·86	295·61	295·23 ₅	$f(4)-f(3)$	> 81·28
	{ 4 ...	377·11	376·80	376·95 ₅	$f(5)-f(4)$	> 81·72
D ₃	{ 1 ...	129·28	128·64	131·12 ₅	$f(2)-f(1)$	
	{ 2 ...	214·16	213·96	222·20	$f(3)-f(2)$	> 85·10
	{ 3 ..	300·29	301·06	300·67 ₅	$f(4)-f(3)$	> 86·61
	{ 4 ...	383·58	384·04	383·81 ₅	$f(5)-f(4)$	> 83·14
D ₄	{ 1 ...	131·37	130·88	131·12 ₅	$f(2)-f(1)$	
	{ 2 ...	222·61	221·85	222·23	$f(3)-f(2)$	> 91·11
	{ 2 ...	316·41	317·14	316·77 ₅	$f(4)-f(3)$	> 94·54
	{ 4 ...	407·36	406·94	407·15	$f(5)-f(4)$	> 90·38
D ₅	{ 1 ...	149·41	148·42	148·91 ₅	$f(2)-f(1)$	
	{ 2 ...	245·40	245·89	245·64 ₅	$f(3)-f(2)$	> 96·73
	{ 3 ...	346·75	345·78	346·26 ₅	$f(4)-f(3)$	> 100·62
	{ 3 ...	434·30	434·82	434·56	$f(5)-f(4)$	> 88·30
D ₆	{ 1 ...	185·15	185·54	185·35	$f(2)-f(1)$	
	{ 2 ...	289·20	288·38	288·79	$f(3)-f(2)$	> 103·44
	{ 3 ...	393·17	392·21	392·69	$f(4)-f(3)$	> 103·90
	{ 4 ...	495·03	495·85	495·44	$f(5)-f(4)$	> 102·75
D ₇	{ 1 ...	248·52	248·19	248·35	$f(2)-f(1)$	
	{ 2 ...	358·67	357·51	358·09	$f(3)-f(2)$	> 109·74
	{ 3 ...	470·44	470·42	470·43	$f(4)-f(3)$	> 112·34
	{ 4 ...	583·63	584·47	584·05	$f(5)-f(4)$	> 113·62

perpendicular to the line joining the nuclei, h is Planck's constant, and c the velocity of light. The values of I' and I'' thus calculated are assembled in columns 10 and 11 of Table VI., while the values of ν_0 as derived from the $P(2)$, $Q(1)$, and $R(1)$ members of each band are placed in columns 1, 2, and 3 of that table. The values of P and ρ are shown in columns 8 and 9.

It will be seen from Table VI. that the initial moment of inertia is larger than the final moment of inertia, and that it begins with a high value at D_1 and then steadily decreases as we go to D_7 . The highest value of the initial moment of inertia is 9.01×10^{-41} gm. cm.², and the lowest value is 5.34×10^{-41} gm. cm.². These two extreme values are nearly equal to those of some of the systems developed by Prof. O. W. Richardson in his recent paper "Structure," Part V. In that paper the maximum value of the moment of inertia of the excited hydrogen molecule (H_2) is found to be 11.35×10^{-41} gm. cm.² for an excited state for which the electron total quantum number is 5. These values are in the neighbourhood of Dieke's * value, which is about 8.2×10^{-41} gm. cm.². When the hydrogen molecule rotates in larger orbits as a result of it being greatly excited, it is quite reasonable to expect that it will have a large moment of inertia. In fact, Takahashi † has obtained a value as high as 20×10^{-41} gm. cm.² for the moment of inertia of an excited H_2 . Again, it may be pointed out that such high values of the moment of inertia of (H_2) fit well with the results expected according to the Quantum theory of specific heat of hydrogen recently discussed by Van Vleck ‡.

From the above discussion it appears that the emitter of the bands set forth in the present paper is an excited hydrogen molecule (H_2). It appears from the majority of values of P and ρ that these bands are not of the half-quantum type. There are indications of a similar group of bands in the blue region of the spectrum having moments of inertia of the order involved in these bands. They are under investigation, and it is hoped to deal with them in another communication.

In conclusion, I should like to express my indebtedness to Prof. O. W. Richardson for suggesting this problem to me,

* Proc. Amsterdam Acad. Sci. xxvii. p. 490 (1924).

† Jap. Journ. Phys. ii. p. 95 (1923).

‡ Phys. Rev. xxviii. p. 995 (1926).

TABLE VI.—Band Constants.

Band.	ν_0 from Q(1).	ν_0 from P(2).	ν_0 from R(1).	F(2).	F(1).	f(2).	f(1).	P.	ρ .	Initial Moment of Inertia, $I' \times 10^{-41}$ gm. cm. ² .	Final Moment of Inertia, $I'' \times 10^{-41}$ gm. cm. ² .
D ₁	17162.57	17162.39	17163.15	201.70	74.88	256.40	98.12	-0.56	-0.62	9.01	7.43
D ₂	17282.44	17282.19	17282.25	151.13	41.97	193.80	57.58	-0.114	-0.193	8.21	6.89
D ₃	17420.02	17420.31	17420.32	136.05	31.52	172.94	44.01	+0.072	-0.018	7.55	6.51
D ₄	17569.96	17570.42	17570.14	133.85	23.66	170.83	39.49	+0.194	+0.074	6.73	6.01
D ₅	17734.28	17734.87	17734.89	165.87	40.29	202.85	53.85	+0.028	-0.064	6.16	5.55
D ₆	17919.80	17919.25	17919.25	232.12	69.52	271.90	86.51	-0.209	-0.294	5.83	5.36
D ₇	18125.20	18125.20	18125.34	375.30	148.05	413.50	163.31	-0.689	-0.719	5.34	4.94

and for his encouragement and helpful criticism during the progress of this work.

Note added.—The following substitutions should be made in the wave-numbers of the band lines in the present paper in the light of the wave-length tables recently published by Gale, Monk, & Lee (*Astr. Phy. Journ.*, March 1928, pp. 89–113).

Substitute	In place of	Remarks.
R (3) 17318·03 (<i>o</i>)	D ₁ R (3) 17318·72 (<i>o</i>)	17318·72, resolved by G. M. & L.
P (5) 16774·42 (6)	D ₂ P (5) 16774·72 (8)	16774·72, resolved by G. M. & L.
Q (1) 17404·90 (<i>o</i>)	D ₃ Q (1) 17407·53 (<i>o</i>)	
R (1) 17508·99 (5) C.D. ++	D ₃ R (1) 17512·36 (<i>o</i>)	
R (4) 17624·43 (<i>o</i>) Lee	D ₃ R (4) 17623·32 (1)	
Q (4) 17457·57 (<i>oo</i>)	D ₄ Q (4) 17458·78 (1)	17458·78, resolved by G. M. & L.
Q (5) 17407·51 (<i>o</i>)	D ₄ Q (5) 17404·99 (<i>o</i>)	
R (3) 17964·86 (1)	D ₅ R (3) 17966·00 (2)	17966·00, resolved by G. M. & L.
P (2) 17717·06 (3)	D ₆ P (2) 17716·87 (3)	17716·87, resolved by G. M. & L.
P (4) 17459·76 (2)	D ₆ P (4) 17458·78 (1)	17458·78, resolved by G. M. & L.
Q (3) 17853·78 (1)	D ₆ Q (3) 17850·99 (3)	
R (2) 18142·91 (1)	D ₆ R (2) 18140·19 (—)	18140·19, resolved by G. M. & L.
R (2) 18416·59 (<i>o</i>)	D ₇ R (2) 18417·19 (<i>rd</i> ²)	18417·19, resolved by G. M. & L.

Prof. Richardson states that there are no interferences between the strong lines of these bands and those of the unpublished extension of the New Bands in the Violet (see Richardson, *R. S. Proc. A*, vol. cxv. p. 528 (1927), Richardson & Davidson, ‘*Nature*,’ June 30, 1928).

XLVIII. *Acoustics of Strings struck by a Hard Hammer.*
By P. DAS and S. K. DATTA*.

IN the *Philosophical Magazine* for March 1928, Dr. Kar and his associates have commented on Das’s † theory of struck string and its experimental verification by Datta ‡. The object of the present note is to show that their criticisms are without foundation, being based on misconceptions of theory and faulty experimentation.

In the first place they make the statement that the discontinuous changes in the pressure of impact with time are an “assumption” on which Das’s theory is based. This is entirely erroneous, since these are not assumed but are the logical results of rigorous mathematical analysis. Further,

* Communicated by Prof. C. V. Raman, F.R.S.

† P. Das, *Proc. Ind. Ass. Cult. Soc.* vol. vii. pts. i. & ii. (1921).

‡ S. K. Datta, *Proc. Ind. Ass. Cult. Soc.* vol. viii. pt. ii. (1923).

identical results have been obtained by Professor C. V. Raman and Dr. B. Banerjee*, who solved the problem by an independent method. Apart from Datta's work, the experimental determination by George† of the pressure-time curve by the oscillograph method actually reveals these discontinuities, and the careful measurements by George and Beckett‡ of the energy lost by the hammer plotted against the striking-length have been shown by Das§ to be in remarkable agreement with the values calculated from his own formulæ.

In fact, a physical interpretation of these discontinuities can be easily given. When the hammer strikes the string the latter at once acquires the velocity v of the hammer, and the length of string set in motion in time δt is $2c\delta t$, where c =wave-velocity. If ρ be the mass per unit-length of the string, the momentum lost by the hammer in time δt is $2c\delta t\rho v$, so that the pressure at the instant $t=0$ is not zero but $2\rho vc$. When the pulse having velocity v returns to the hammer after reflexion from the nearer extremity, it is again reflected completely from the hammer, since the mass $\rho c\delta t$ of length $c\delta t$ of the string is infinitesimal compared with that of the hammer. The change of momentum in time δt is $\rho c\delta t \cdot 2v$, so that the pressure again increases by $2\rho vc$. This recurs with the period of vibration of the part of the string between the hammer and the nearer fixed end.

Dr. Kar and his co-workers adopt in their experiments a method which they borrow from Datta without acknowledgment. The details of their arrangements are, however, seriously defective. From the diagram and description appearing in their paper, it would seem that the string was stretched on two horizontal bridges and set in motion in a horizontal plane. It is obvious that there would be considerable slipping at the bridges, and the effective vibrating length of the string would be greater than the distance between the bridges. The overtones would be inharmonic, and points on the string usually regarded as nodes would hardly have a nodal character, so that in touching a so-called node the very overtone of which the amplitude is sought, is silenced. Their experimental results are thus unreliable and useless for the purpose of testing a theory. In this connexion we may point out that the large differences which they find in the amplitude of the fundamental with hammers of identical mass and velocity, but of different metals, are

* Raman and Banerjee, Proc. Roy. Soc. A, vol. xevii. (1920).

† W. H. George, Proc. Roy. Soc. A, vol. cviii. p. 284 (1925).

‡ George and Beckett, Proc. Roy. Soc. A, vol. cxiv. p. 111 (1927).

§ P. Das, Ind. Journ. Phys. vol. i. pt. iv. (1927).

doubtless spurious. George and Beckett*, in their recent very careful and accurate work did not find any notable changes in amplitude, either of the fundamental or of the overtones with hammers of different materials.

In calculating the amplitude of the harmonics, the upper limit T of the integral

$$\int_0^T F_{\cos}^{\sin} n(t-t') dt' \quad [F = \text{pressure}]$$

was taken by Datta to be the intercept between $t'=0$ and the point where the pressure-time curve cuts the t' -axis. This procedure, which is questioned by Kar, is obviously justifiable. For, at the moment the contact between the string and the hammer ceases, the pressure F becomes zero. It is only if repeated contacts occur that such a procedure would be inadequate, and such cases have not so far been theoretically treated.

Finally, as an illustration of the imperfect appreciation of theory shown by Kar and his colleagues, we may refer to the paragraph (Phil. Mag. vol. v. p. 556, 1928) in which they express impulse in terms of grammes weight, and thus confuse its dimensions with those of force.

210 Bowbazar Street,
Calcutta,
25th April, 1928.

XLIX. *Magnetic Studies on Salts, with Particular reference to those with Complex Ions.* By LARS A. WELO (*The Rockefeller Institute for Medical Research*) †.

THIS paper is intended to be mainly a descriptive rather than an interpretative account of a study of the magnetic properties of a very large number of salts of various types. It seems, therefore, best to consider the results by groups according to the principal features which have been observed. A discussion of the significance of the results, in so far as a discussion seems possible or may be ventured upon, will then be given along with the appropriate experimental data.

* George and Beckett, Proc. Roy. Soc. A, vol. cxvi. p. 126 (1927).

† Communicated by the Author.

The salts, 124 in number, will be considered under the following main headings :—

1. Polynuclear salts of iron and chromium having very large negative values of θ in the Curie-Weiss law $K_a(T - \theta) = C$.
2. Iron salts having irregular and variable moments within the observed range of temperatures.
3. Miscellaneous salts of iron and chromium of normal ionic moment and with relatively small values of θ in the Curie-Weiss law.
4. Coordination compounds of chromium and cobalt previously studied by Rosenbohm at only one temperature.
5. A ferricyanide and the penta-cyano derivatives.
6. The Prussian blues.
7. Salts showing an anomalous temperature variation of the susceptibilities.
8. Diamagnetic and near diamagnetic salts of some transition elements.

GENERAL DISCUSSION OF THE METHODS EMPLOYED.

All of the salts were studied in the solid state in the form of powders. In the case of the paramagnetic substances, this necessitates susceptibility measurements throughout a range of temperature sufficient to make certain that $\frac{1}{K_a} = f(T)$ is linear, and to permit the determination of the constants C and θ with the required accuracy. The apparatus was modelled after that described by Foëx and Forrer *, and need not be described in detail here. The magnetic field in the region occupied by the specimen was about 4000 gauss. As a rule, determinations of the susceptibilities were made at three temperatures: when the salt was at room temperature; when it was surrounded by melting ice; and when it was surrounded by solid CO_2 . The refrigerants were contained in the space between two coaxial glass tubes joined at one end. The real temperatures attained by the salts were not actually measured. This fact raises two questions. Does a specimen acquire a definite temperature each time that it is surrounded by the refrigerant, and, if so, by how much does this temperature differ from the actual temperature of the refrigerant? The first question was answered by comparing the values of θ

* Foëx & Forrer, *Journ. de Phys. et le Rad.* vii. p. 180 (1926).

obtained with a given salt in separate runs. Throughout the work many such were made. It was found that for values of θ not far from zero, they agreed within 2°C .

on the average. From the geometry of $\frac{1}{K_a} = f(T)$, it was calculated that with ice as a refrigerant the temperatures acquired by the salts were always the same to within 0.18°C ., and with solid CO_2 as a cooling substance they were constant to within 0.65°C .

A direct thermocouple determination of the difference between the temperature acquired by a sample and that of the solid CO_2 proved it to be 8.5°C . This was checked by measurements on Mohr's salt, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O}$, for which Foëx* has found $\theta = +22^\circ$. Using the nominal temperatures of 0°C . for ice, and -78.5°C . for CO_2 , θ appeared, in my measurements, to be -3° . The difference of 25° in θ leads again to a correction of 8.5°C . when solid CO_2 is used. In the same way the correction when ice is used turned out to be 2.4°C . When ice and solid CO_2 were used as cooling substances, the actual temperatures of the salts were therefore $2.4^\circ \text{C} = 275.5^\circ \text{K}$. and $-70^\circ \text{C} = 203.1^\circ \text{K}$., respectively, with the relatively small uncertainties noted in the previous paragraph.

Only very rarely were the ice points omitted and susceptibilities observed at only two temperatures. This was done only when the type of salt was one which would certainly give a linear $\frac{1}{K_a} = f(T)$. The value of the moment observed served as a reliable check. A few salts were also studied at temperatures above that of the room by the use of a small electric furnace.

Mohr's salt, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O}$ served as a standard. Its magnetic constants have been carefully determined by Foëx†, so that its susceptibility at the calibration temperature can be calculated. The susceptibility values of Foëx agree with the Leiden data on the same salt to within 0.4 per cent. when adjusted to the same temperature. A further check on the standard was obtained by measuring $\text{Fe}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O}$ in terms of it. The susceptibility observed was in essential agreement with the Leiden datum for this ferric salt. As a standard, Mohr's salt has the additional advantage of being uniform throughout a sample.

* Foëx, *Ann. de Phys.* xvi. p. 259 (1921).

† *Loc. cit.*

Commercial samples of CoCl_2 and NiCl_2 were seriously lacking in this respect.

The susceptibilities are given by the formula

$$K = \frac{v-v'}{v_1-v'} \frac{m_1}{m} \left(K_1 - \frac{k_a}{\delta_1} \right) + \frac{k_a}{\delta},$$

where

v = millivolts observed with specimen. (The compensating current was measured by a millivoltmeter used in connexion with a properly adjusted shunt.)

v_1 = millivolts observed with standard.

v' = millivolts observed with empty container (slight temperature variation known).

m and m_1 = the masses of the substance and standard, respectively.

δ and δ_1 = the densities of the substance and standard, respectively.

K_1 = susceptibility of the standard.

k_a = volume susceptibility of air.

Except for the very weak paramagnetics, the air correction is negligible and the formula reduces to

$$K = \frac{v-v'}{v_1-v'} \frac{m_1}{m} K_1.$$

The gram atomic susceptibilities are given by

$$K_a = KM - k_d,$$

where

M = molecular weight.

k_d = sum of gram atomic susceptibilities of constituents other than iron, chromium, cobalt, etc., as the case may be.

A list of the gram atomic susceptibilities of the constituents involved throughout the work may well be included here. Practically all are due to Pascal*.

C = -6.0×10^{-6}	Cl = -20.0×10^{-6}
H = -2.9×10^{-6}	Br = -31.0×10^{-6}
O = -4.6×10^{-6}	I = -45.0×10^{-6}
S = -15.0×10^{-6}	Na = -9.2×10^{-6}
N = -5.5×10^{-6}	K = -18.5×10^{-6}
Ca = -15.8×10^{-6}	

* Pascal, 'Revue Générale des Sciences,' July 15, 1923.

The following values were used for certain groups:—

$$\text{H}_2\text{O} = -13.0 \times 10^{-6},$$

$$\text{NO} = -1.6 \times 10^{-6},$$

$$\text{and } \text{PO}_4 = -33.5 \times 10^{-6}.$$

Each time that the group CN occurs, a correction of $+0.8 \times 10^{-6}$ was applied. In some salts, Co and Cr appear in near diamagnetic ions. The values used were $+55.0 \times 10^{-6}$ and $+63.0 \times 10^{-6}$, respectively. According to Pascal, the atomic susceptibility of oxygen is to be taken as a variable in accordance with the nature of the chemical bonds. This variation is small, however, and was neglected in all paramagnetic salts.

The diamagnetic and near-diamagnetic salts were studied by the Gouy method, the forces being measured with a sensitive balance. The fields were about 11,000 gauss. The formula is the same as before, v , v_1 , and v' being replaced by f , f_1 , and f' . Water was used as a standard with $K_1 = -0.719 \times 10^{-6}$. With diamagnetic salts the air correction is not negligible. The density, if unknown, was taken to be that of a mixture of bromoform and benzene, in which the salt would just float. This procedure in the determination of the densities is rough, but permissible since the correction terms are small. The chief drawback with the Gouy method when applied to powders is that of obtaining uniform packing. Several measurements were necessary, repacking each time. To give the reader an idea of the accuracy attained with the diamagnetic salts, the table contains also the number of measurements made and the probable error,

$$E = \pm \frac{0.85}{n \sqrt{n-1}}.$$

The tables of data on the paramagnetic salts contain the specific susceptibilities adjusted to a temperature of 20°C . by means of the relation $K_a(T - \theta) = C$ with the values of C and θ as tabulated. The accuracy implied by the use of the second decimal place was not actually attained, even relatively. On the other hand, rounding off K to the first decimal place would not do justice to the relative accuracy of the measurements at the different temperatures as indicated by the closeness with which the points fall on straight lines in the plots of $\frac{1}{K_a}$ against T . Following the usual custom, the Weiss magneton numbers are also

tabulated as calculated by $p=14.07 \sqrt{C}$. The values of C and θ were computed by selecting any two temperatures, T_1 and T_2 , and observing the corresponding values of $\frac{1}{K_a}$ directly from the graphs of $\frac{1}{K_a}=f(T)$. It is readily seen that

$$C = \frac{T_1 - T_2}{\frac{1}{K_{a1}} - \frac{1}{K_{a2}}}$$

and

$$\theta = \frac{T_2 K_{a2} - T_1 K_{a1}}{K_{a2} - K_{a1}}.$$

I. Polynuclear Salts of Iron and Chromium with Large Negative Values of θ .

These unique and interesting salts, listed in Tables I., II., and III., were very kindly supplied by Professor R. Weinland, of the University at Würzburg *. All are acetates except Nos. 7 and 8 which are benzoates, Nos. 23 and 24 which are formates, No. 9 which contains pyrogallol groups, No. 10 which is a salicylate and No. 25 which is a propionate. The salts that were analysed for iron at this Institute at about the time of the magnetic measurements are indicated under "Remarks."

The results of the magnetic measurements are shown in Tables I., II., and III. and in figs. 1 and 2. Some of the salts listed in Table II. do not appear in fig. 2. To plot the values obtained would result in the superposition of, and confusion among, the lines. Likewise the curves obtained with the salts listed in Table III. are omitted. In all these omitted cases, the curves $\frac{1}{K_a}=f(T)$ were straight lines.

It appears that the iron and chromium ions in salts of this type have associated with them the normal values of C and p . The only clear-cut exception is the pyrogallol salt No. 9. It may be noted that this salt lacks the OH group which appears either once or twice in salts giving uniformly normal

* For a general index to the literature regarding salts of this type, see Professor Weinland's book, 'Einführung in die Chemie der Komplex-Verbindungen,' Stuttgart, 1919, pp. 345 ff. Particular papers that may be mentioned are: *Berichte*, xlii. p. 3881 (1909), xlv. p. 2662 (1912), and xlvii. p. 2753 (1914); *Zeit. anorg. Chem.* xcii. p. 81 (1915); cli. p. 271 (1926) and clii. p. 1 (1926). Also *Ann. der Chemie*, ed. p. 219 (1913).

TABLE I.—Polynuclear Salts of Iron.

Reference No.	SALT.	$K \times 10^6$ (20° C.).	C.	θ .	p .	Re- marks.
1	$\frac{1}{3}[\text{Fe}_3(\text{CH}_3\text{COO})_6(\text{OH})_2]\text{NO}_3 + \frac{5}{3}\text{H}_2\text{O}$	19.13	4.10	-577	28.5	
2	$\frac{1}{3}[\text{Fe}_3(\text{CH}_3\text{COO})_6(\text{OH})_2]\text{Cl} + \frac{7}{3}\text{H}_2\text{O}$	18.17	3.97	-603	28.0	Anal.
3	$\frac{1}{3}[\text{Fe}_3(\text{CH}_2\text{CNCOO})_6(\text{OH})_2]\text{ClO}_4 + \frac{8}{3}\text{H}_2\text{O}$	14.59	4.26	-607	29.0	
4	$\frac{1}{3}[\text{Fe}_3(\text{CH}_2\text{ClCOO})_6(\text{OH})_2]\text{NO}_3 + \frac{5.5}{3}\text{H}_2\text{O}$	14.38	4.05	-593	28.3	Anal.
5	$\frac{1}{3}[\text{Fe}_3(\text{CCl}_3\text{COO})_6(\text{OH})]$	9.27	4.05	-553	28.3	Anal.
6	$\frac{1}{3}[\text{Fe}_3(\text{CH}_3\text{COO})_6](\text{CH}_3\text{COO})_2(\text{FeBr}_4)$	27.90	3.64	- 89	26.8	Anal.
7	$\frac{1}{3}[\text{Fe}_3(\text{C}_6\text{H}_5\text{COO})_6(\text{OH})](\text{C}_6\text{H}_5\text{COO})(\text{ClO}_4) + \frac{1}{3}\text{H}_2\text{O}$	11.22	4.40	-695	29.5	
8	$\frac{1}{3}[\text{Fe}_3(\text{C}_6\text{H}_5\text{COO})_3\text{O}(\text{OH})_3]\text{C}_6\text{H}_5\text{COO}$	28.00	1.74	+ 37	18.6	
9	$\frac{1}{3}[\text{Fe}_3(\text{C}_6\text{H}_5\text{O}_3)_5]\text{H}_6(\text{NH}_3)_3 + \frac{8}{3}\text{H}_2\text{O}$	24.58	3.46	-129	26.2	Anal.
10	$\frac{1}{4}[\text{Fe}_3(\text{C}_6\text{H}_4(\text{OH})\text{COO})_6(\text{OH})][\text{Fe}(\text{C}_6\text{H}_4(\text{O})\text{COO})_2]\}$ $\text{C}_6\text{H}_4(\text{OH})\text{COO} + \frac{8.5}{4}\text{H}_2\text{O}$	35.64	4.20	+ 6	28.8	Anal.

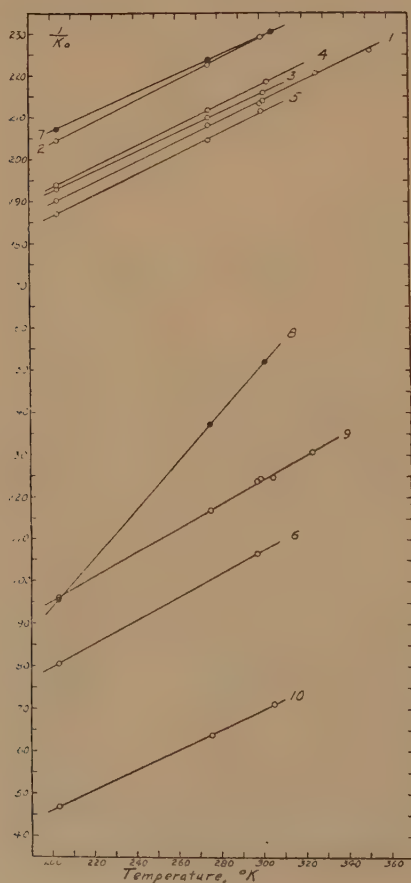
TABLE II.—Polynuclear Salts of Chromium.

Reference No.	SALT.	$K \times 10^6$ (20° C.).	C.	θ .	p .	Re- marks.
11	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})_2]\text{Cl} + \frac{8}{3}\text{H}_2\text{O}$	20.35	1.92	- 93	19.5	
12	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})_2\{\text{CS}(\text{NH}_2)_2\}_3]\text{Cl} + \frac{3}{3}\text{H}_2\text{O}$	16.54	1.93	-103	19.5	
13	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})_2(\text{NH}_3)_3]\text{I}$	19.10	1.92	-116	19.5	
14	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})_2\text{NH}_3]\text{CH}_3\text{COO}$	22.95	1.91	-103	19.4	
15	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})_2\text{CNS}] + \frac{3}{3}\text{H}_2\text{O}$	21.77	1.91	-101	19.4	
16	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})_2\{\text{CO}(\text{NH}_2)_2\}_2]\text{Cl} + \frac{1}{3}\text{H}_2\text{O}$..	20.08	1.87	- 89	19.2	
17	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})_2(\text{C}_5\text{H}_5\text{N})_3]\text{NO}_3$	16.40	1.85	-100	19.1	Anal.
18	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})](\text{CH}_3\text{COO})_2 + \frac{2}{3}\text{H}_2\text{O}$	21.38	1.97	-106	19.7	
19	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})](\text{NO}_3)(\text{CH}_3\text{COO}) + \frac{2.5}{3}\text{H}_2\text{O}$..	20.50	1.95	-111	19.6	
20	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})]\text{Cl}(\text{CH}_3\text{COO}) + \frac{4}{3}\text{H}_2\text{O}$	20.37	1.91	-105	19.4	
21	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6](\text{CrO}_4)(\text{CH}_3\text{COO}) + \frac{4.5}{3}\text{H}_2\text{O}$	19.23	2.06	-120	20.2	
22	$\frac{1}{3}[\text{Cr}_2(\text{CH}_3\text{COO})_6](\text{Cr}_2\text{O}_7)(\text{CH}_3\text{COO}) + \frac{2}{3}\text{H}_2\text{O}$	18.15	1.93	- 92	19.5	
23	$\frac{1}{3}[\text{Cr}_3(\text{HCOO})_6(\text{OH})_2]\text{HCOO} + \frac{5}{3}\text{H}_2\text{O}$	25.08	2.02	-108	20.0	
24	$\frac{1}{3}[\text{Cr}_3(\text{HCOO})_6(\text{OH})_2]\text{Cl} + \frac{5}{3}\text{H}_2\text{O}$	24.60	1.88	- 93	19.3	
25	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{CH}_2\text{COO})_6(\text{OH})_2]\text{Cl} + \frac{5}{3}\text{H}_2\text{O}$	18.81	1.97	-114	19.7	
26	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})_3] + \frac{1.2}{3}\text{H}_2\text{O}$	21.55	1.92	- 44	19.5	
27	$\frac{1}{3}[\text{Cr}_3(\text{CH}_3\text{COO})_{4.5}(\text{OH})_{4.5}] + \frac{1.4}{3}\text{H}_2\text{O}$	24.00	1.79	+ 1	18.8	
28	$\text{Cr}(\text{CH}_3\text{COO})_3$	22.28	1.83	- 60	19.0	Anal.

TABLE III.—Mixed Polynuclear Salts.

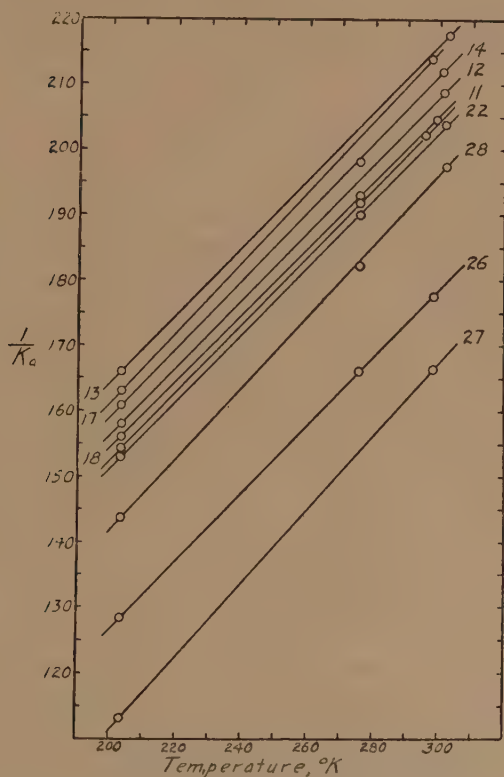
Reference No.	SALT.	$K \times 10^6$ (20° C.).	C.	θ .	p .
9	$[\text{Cr}_2\text{Fe}(\text{CH}_3\text{COO})_6(\text{OH})_2]\text{Cl} + 6\text{H}_2\text{O}$	16.80	8.00	—380	—
30	$[\text{Cr}_2\text{Fe}(\text{CH}_3\text{COO})_6(\text{OH})_2]\text{NO}_3 + 6\text{H}_2\text{O}$	17.15	9.38	—453	—
31	$[\text{Fe}_2\text{Cr}(\text{CH}_3\text{COO})_6(\text{OH})_2]\text{NO}_3 + \text{H}_2\text{O}$	18.81	7.69	—342	—

Fig. 1.



values of C and p and large negative values of θ . No significance can at present be attached to the salts No. 6 and No. 8. They are included in the table only as interesting variants. Structure complications make it difficult to decide just how to handle these two salts. For example, the measurements on No. 6 were handled on the questionable assumption that the contribution of the negative ion FeBr_4

Fig. 2.



is nothing. The low values of C and p given for No. 8 are probably related to the peculiar position of the oxygen as the salt is formulated. Not enough of salt No. 8 was at hand to make an analysis for iron. In view of the general excellence of the other salts as indicated by the agreement of our iron analyses with the formulæ and published analyses, it is felt that the low values of C and p are not due to deficiency in iron.

In Table III. the C values apply to the whole trinuclear complex ion, and the p -values are omitted. In salt No. 29 (for analysis see *Berichte*, xlii. p. 3881 (1909)), C is approximately the sum of the normal values of C for the ferric and chromic ions. Assume $C=4.25$ for the ferric ion. For each chromic ion $C = \frac{8.00 - 4.25}{2} = 1.87$, leading to $p=19.2$,

which is in close agreement with $p=19.0$ as observed in simple chromium salts. A similar additive distribution is not possible for Nos. 30 and 31. No analyses on these salts could be found in the literature, and my own attempts to analyse the small quantities available failed. The probabilities are that the proportions of iron and chromium are not as formulated. Otherwise, we should have to conclude that the additive relations of the Curie constant observed when only iron or only chromium are the metals present, as in the salts of Tables I. and II., do not hold for the mixtures; and that the additivity observed with salt No. 29 is only a coincidence. The only thing that can be said, with certainty, about the mixed salts of Table III. is that the values of θ are negative and large, and intermediate between those found with iron alone and chromium alone.

Rosenbohm* has measured four hexa-formates of chromium of the type listed in Table II. at one temperature only. Jackson† recently considered these data, and tried to account for the apparent low moments by assuming that only two of the three chromium ions have the normal moment of 19 magnetons. The third chromium ion was assumed to be in another state of zero moment. Such an assumption is not necessary, in view of the results shown in Table II. To this Jackson has agreed in a private communication after having been informed of the present results.

The striking thing about these salts is, of course, the values of θ of the order -600 in the iron salts and -100 for those containing chromium. The problem of negative values of θ and of negative molecular fields is an old one and appears here in a particularly pressing form. They do not appear to be directly related to the existence of polynuclear ions. This possibility is eliminated by the fact that θ is only -129 in the pyrogallol salt, No. 9, and is $+6$ in the salicylate, No. 10; provided we accept the formulations given as representing their real nature. This consideration eliminates also a relation between θ and the

* Rosenbohm, *Zeit. f. Phys. Chem.* xciii. p. 711 (1919).

† Jackson, *Phil. Mag.* iv. p. 1070 (1927).

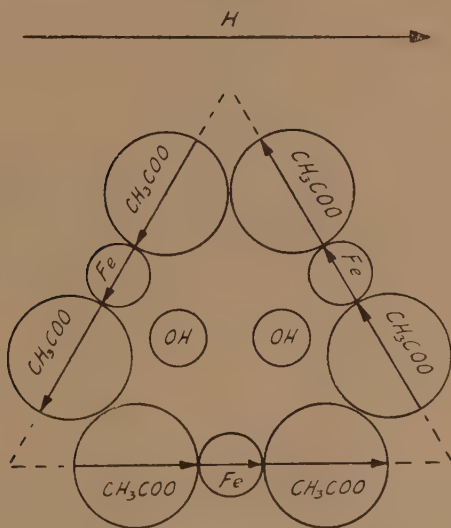
mass of the whole complex ion. Such a relation would be contrary to the theory of Oosterhuis *, if we are permitted to associate with J in his expression

$$\theta = \frac{-h^2}{24\pi^2 JK}$$

the moment of inertia of the whole complex ion. According to this theory, we should observe small values of θ in salts with large complex ions.

A possible way out is open to us if we recognize that the organic groups, CH_3COO , CHOO , $\text{C}_6\text{H}_5\text{COO}$, etc., are

Fig. 3.



themselves very probably permanent electric dipoles. We may then adopt and modify a point of view due to Debye †, which involves the assumption that the elementary magnets, that is, the iron and chromium ions, have permanent electric moments as well.

Let us consider as an example the typical polynuclear salt No. 1 $[\text{Fe}_3(\text{CH}_3\text{COO})_6(\text{OH})_2]\text{NO}_3 + 6\text{H}_2\text{O}$, and represent the complex ion by a model as in fig. 3. Since it is a plane

* Oosterhuis, Comm. Phys. Lab. Leiden, No. 31; Amst. Acad. p. 217, June 1913.

† Debye, *Handbuch der Radiologie*, Marx, Leipzig, 1925, vol. vi. p. 704 ff. Also 'Kinetic Theory of Gases', Loeb, New York, 1927, p. 430.

model, it does not represent the true relative positions of the various parts, but it does serve to visualize the electrostatic control on the ferric ions. The model, as drawn, meets the requirement, however, of having no external resultant moment, either magnetic or electric. The complex ion as a whole, being fixed in the crystal lattice, does not rotate, but we shall adhere to the classical view that the ferric ions are capable of orientation by magnetic and electric fields. The magnetic axes of the ferric ions, which are not indicated in the figure, may or may not coincide with the permanent electric polarization.

It is immediately evident that the magnetization

$$I = N\mu_m \overline{\cos \phi}$$

induced by the magnetic field H and hence the susceptibility,

$$\frac{N\mu_m \overline{\cos \phi}}{H},$$

must be less than if there were no electrostatic control by the neighbouring organic groups. Consider salt No. 1 as an example. The gram atomic susceptibility was, at 20°C .

$$K_a = \frac{C}{T - \theta} = \frac{4.10}{293 + 577} = \frac{4.10}{870} = 4715 \times 10^{-6}.$$

A simple ferric salt having $\theta = 0$ and with the same Curie constant would have given

$$K_a = \frac{4.10}{293} = 14000 \times 10^{-6}.$$

The electrostatic control on the ferric ions in the case of the complex salt being considered has reduced the mean special value of $\overline{\cos \phi}$ to

$$\frac{4715 \times 10^{-6}}{14000 \times 10^{-6}} = 0.33 \text{ of its uncontrolled value.}$$

A similar calculation applied to a chromium salt, say, No. 11 $[\text{Cr}_3(\text{CH}_3\text{COO})_6(\text{OH})_2]\text{Cl} + 8\text{H}_2\text{O}$, shows that the postulated electrostatic control has reduced the susceptibility to 0.76 of its value without the control. A weaker control is indicated for the chromic ion, due presumably to a smaller electric moment μ_e .

Another question which must be considered is the influence of electrostatic control on the disorganization due to temperature agitation. The magnitude of the control is itself a

function of the temperature, owing to fluctuations in position and orientation of the controlling organic groups. But in any event the control which resists disorganization by temperature is, at every instant, exactly the same as the control which resists organization by the magnetic field. The temperature coefficient of the magnetization, or of the susceptibility, is therefore decreased in the same proportion as the magnetization or the susceptibility. But the temperature coefficient of susceptibility is, by experiment, the quantity $-\frac{1}{T-\theta}$. Hence

$$\frac{K_a}{1 - \frac{1}{T-\theta}} = \text{a constant, which is the Curie-Weiss law.}$$

According to the view presented here, negative values of θ in the law $K_a(T-\theta)=C$ have a distinctly different origin from positive values. If the idea proves to be acceptable, it is of more importance than as a mere device to explain the frequent appearance of negative values. It removes what has been thought to be a difficulty in Debye's interpretation of molecular fields in ferromagnetics as being electric in nature. Debye's expression for ν in the equation for the effective field in ferromagnetics

$$H_e = H + \nu I$$

is
$$\nu = \frac{4\pi}{3} \frac{\mu_e^2}{\mu_m^2}.$$

It is of the observed order of magnitude in ferromagnetics, but cannot explain negative molecular fields or negative values of θ , since $\frac{\mu_e^2}{\mu_m^2}$ is essentially positive. On the view proposed, there are no induced negative molecular fields. The fields which resist magnetization are provided by the permanent electric dipoles already present in the system.

It may be added that the hypothesis which has been briefly outlined provides the forces necessary for the existence of the aggregate of metallic ions and organic and hydroxyl groups which constitute the complex positive ion of the type $[\text{Fe}_3(\text{CH}_3\text{COO})_6(\text{OH})_2]$.

It would be interesting to study the magnetic behaviour of these polynuclear salts in solution, a line of work which I hope soon to undertake.

II. *Iron Salts having Irregular and Variable Moments.*

The results obtained with this group of salts are presented in Table IV. and fig. 4. They are commercial salts except the tetra-eugenol salt, No. 33, and the pyrocatechin salt, No. 34, which were supplied by Professor Weinland*. The work on No. 32 and on Nos. 35 to 39 was suggested by the irregular moments for ferric citrates and phosphates which have been calculated by Weiss from Pascal's measurements†. It was hoped that the values given there might be checked and definitely established. This could not be done, however. Even apparently analogous salts such as iron

TABLE IV.—Iron Salts with Irregular and Variable Moments.

Reference No.	SALT.	$K \times 10^6$ (20° C.).	C.	θ .	p .	Remarks.
32	FePO ₄	71.40	3.82	— 60	27.5	Anal.
33	{ [Fe(C ₆ H ₃ (C ₃ H ₅ OCH ₃ O) ₄] K{C ₆ H ₃ (C ₃ H ₅)(OCH ₃)(OH)} }	15.08	3.83	+ 24	27.5	"
34	[Fe(C ₆ H ₄ O ₂) ₂]K+2.2H ₂ O	33.82	3.56	— 3	26.5	"
	" "	...	2.81	+ 69	23.6	
35	Iron Pyrophosphate.....	20.72	4.81	—185	30.8	Anal.
36	Iron Ammonium Citrate	23.65	3.98	—169	28.0	"
37	Iron Magnesium Citrate	24.65	3.78	—157	27.3	"
38	Iron Potassium Citrate	23.52	2.67	— 24	23.0	"
39	Iron Tartrate and Ammonia	53.40	3.50	+ 63	26.3	"
	" "	...	3.04	+ 93	24.5	
	" "	...	2.66	+123	22.9	

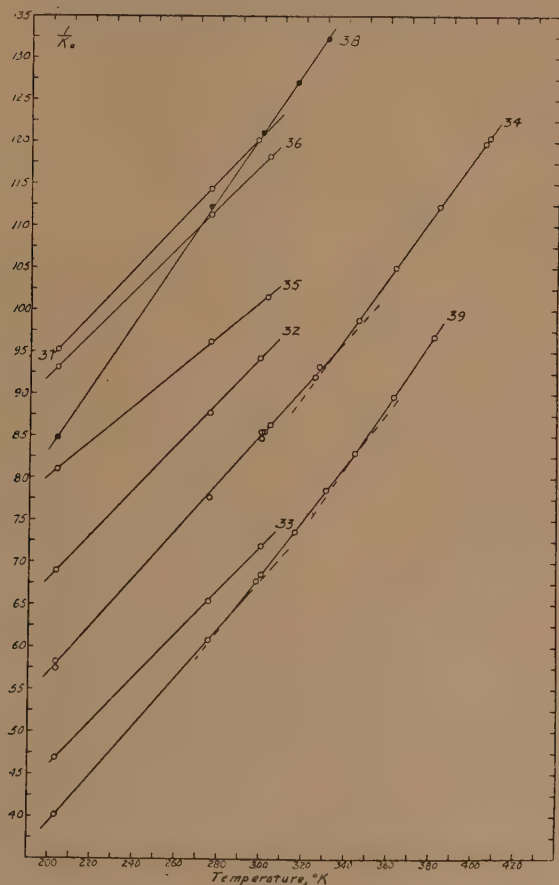
ammonium citrate and iron potassium citrate gave p values of 28 and 23 respectively. It is very doubtful whether these are the actual moments. It is more probable that the ferric ions in the pyrophosphate, the citrates, and the tartrate have the normal p values of about 29, but that the salts are mixtures of two or more components, each component being characterized by different values of θ in $K_a(T-\theta)=C$. Until the number of components and their proportions have been determined by complete chemical analyses, it cannot be stated that the iron does not appear with the

* See *Arch. d. Pharm. cclii.* p. 600 (1914); and *Berichte*, xlv. pp. 148 and 1113 (1912).

† Kunz, "Theories of Magnetism," *Bull. No. 18, Nat. Res. Council*, p. 199.

normal moment of the ferric ion. A determination of iron alone is not sufficient. It should be stated that the salts, No. 32 and Nos. 35 to 39, were each analysed for iron three times by two different methods which checked to within 1 per cent.

Fig. 4.



The pyrocatechin salt undergoes a well-defined and reversible transformation at about $62^{\circ}C$. Considerable arbitrariness is involved in drawing curves through the points observed with iron tartrate and ammonia, and consequently in calculating C , θ , and p . Only the middle range is at all reliable, and here the apparent moment turns out to be far below the normal for ferric ion.

III. *Miscellaneous Salts of Iron and Chromium.*

The salts listed in Tables V. and VI. were, for the most part, obtained from Professor Weinland. The exceptions were the cupferon salt, No. 64, which was prepared by

TABLE V.—Miscellaneous Salts of Iron.

Refer- ence No.	SALT.	K $\times 10^6$ (20° C.).	C.	θ .	p .	Remarks.	
40	[Fe(HCOO) ₂]Cl + H ₂ O	60.17	4.18	—	55	28.8	Anal., formate.
41	[Fe(SO ₄) ₃]Na ₃ + 3H ₂ O	30.44	4.15	+	5	28.6	Anal.
42	[Fe(SO ₄) ₂]NH ₄	50.72	4.00	—	2	28.1	
43	[Fe(PO ₄) ₂]H ₃ (NH ₃) ₃ + $\frac{7}{3}$ H ₂ O	41.58	4.17	—	42	28.7	
44	[Fe(PO ₄) ₃]H ₅ Na	32.35	4.15	—	52	28.6	Anal.
45	[Fe(PO ₄) ₂]H ₃ (NH ₃)	46.70	3.97	—	25	28.0	
46	Fe(H ₂ PO ₂) ₃	57.30	4.07	+	12	28.4	Hypophosphite.
47	[Fe(C ₆ H ₃ (CHO)(OCH ₃)O) ₅]K ₂ + H ₂ O ...	17.15	4.33	+	23	29.2	Vanillin.
48	[Fe(CrO ₄) ₂]K + 2H ₂ O	39.44	4.12	+	4	28.5	
49	[Fe(C ₆ H ₄ O ₂) ₃]K ₃ + 2H ₂ O	26.92	4.00	+	20	28.2	Pyrocatechin.
50	[FeF ₆]Na ₃	52.25	4.15	—	119	28.6	M=191.
51	[FeF ₅ OH ₂]H ₂ (CN ₃ H ₅) ₂ + 3H ₂ O	41.95	3.97	+	22	28.0	Anal., guanidine.
52	[Fe(SO ₄) ₂]H(C ₅ H ₅ N) + 2H ₂ O	39.15	3.96	+	18	28.0	Pyridine.
53	[FeCl ₂ (C ₂ O ₄)]H(C ₅ H ₅ N)	40.00	4.13	—	65	28.6	M=286.
54	[FeSO ₄ (C ₂ O ₄)]H ₃ (C ₅ H ₅ N) ₂	28.90	4.07	—	22	28.4	M=440.
55	[Fe(OH ₂) ₂ (C ₂ O ₄) ₂]H(C ₅ H ₅ N)	42.30	4.07	+	19	28.4	Anal.
56	[FeCl(OH ₂)(C ₂ O ₄) ₂]H ₃ (C ₅ H ₅ N) ₂	32.12	3.98	+	19	28.1	Anal.
57	[Fe(CH ₃ COCHCOCH ₃)(C ₅ H ₅ N) ₂]Cl ₂ ...	37.92	4.15	+	12	28.6	Acetyl acetate, pyridine.
58	[Fe(OH ₂) ₂ (CH ₂ C ₂ O ₄) ₂]H(C ₅ H ₅ N) + 2H ₂ O	35.60	4.05	+	20	28.3	Malonate.
59	$\frac{1}{2}$ [Fe ₂ Cl ₉]H ₃ (C ₅ H ₅ N) ₃	43.30	4.03	+	19	28.2	
60	[Fe(CrO ₄) ₆]H ₉ (C ₅ H ₅ N) ₃	15.20	4.33	+	6	29.2	
61	[Fe(ClO ₄) ₃](C ₁₁ H ₁₂ N ₂ O) ₆	9.42	4.05	+	20	28.3	Antipyrine.
62	[FeCl ₃](C ₁₁ H ₁₂ N ₂ O) _{1.5}	33.34	4.30	+	12	29.1	Anal.
63	[FeSO ₄ (C ₂ O ₄)]H(C ₉ H ₇ N)	29.50	4.23	—	91	28.9	Anal., quinoline.
64	Fe(C ₆ H ₅ N ₂ O) ₈	31.92	4.29	—	9	29.1	M=441, cupferron.
65	Fe(CH ₃ COCHCOCH ₃) ₃	42.22	4.20	+	14	28.8	Acetyl acetate.
66	[Fe(C ₆ H ₄ (O)COO) ₂]K + 4H ₂ O	32.17	4.20	0		28.8	Salicylate.
67	Fe(C ₆ H ₅ (NOH)CO) ₃ + $\frac{3}{2}$ H ₂ O	28.75	4.21	0		28.8	Benzhydroxamate.
68	Fe(C ₆ H ₅ O ₂) ₃	38.88	4.15	0		28.6	Valerate.
69	[Fe(C ₆ H ₄ (CO) ₂ C ₆ H ₂ O ₂) ₃](NH ₄) ₃	16.55	4.12	0		28.5	Anal., alizarine.
70	FeC ₂ O ₄ + 2H ₂ O	68.80	3.33	+	26	25.7	Anal., ferrous oxalate.
71	Fe(ClO ₄) ₂ + 6 $\frac{2}{3}$ H ₂ O	29.30	3.26	+	1	25.4	Anal., ferrous perchlorate.
72	Fe(C ₄ H ₃ O ₃) ₂ + $\frac{5}{2}$ H ₂ O	41.27	3.41	0		26.0	Anal., ferrous lactate.

Dr. Baudisch, the chromium salts Nos. 73, 78, and 79, loaned by Dr. Hendricks, and Nos. 46, 68, 70, 71, and 72,

which were of commercial origin. The plots of $\frac{1}{K_a} = f(T)$

are not shown. In each case where observations were made at various temperatures the relation was linear. Only in the cases of salts Nos. 66, 67, 68, 69, and 72 was a study of the temperature variation of the susceptibility omitted. The recorded values of $\theta=0$ are, therefore, not observed values, but were assumed. This assumption is justified by the fact that the values of C and p are the normal values of the type of ion involved.

TABLE VI.—Miscellaneous Chromic Salts.

Reference No.	SALT.	$K \times 10^6$ (20° C.).	C .	θ .	p .
73	$K_3Cr(CN)_6$	18.84	1.73	+17	18.5
74	$[Cr(C_2O_4)_3]K_3 + 3H_2O$	12.56	1.77	+12	18.7
75	$[Cr(OH_2)_6]Cl(SO_4) + 2H_2O$	19.86	1.87	+13	19.2
76	$[Cr(OH_2)_6Cl]SO_4 + 3H_2O$	19.62	1.84	+15	19.0
77	$[Cr(NH_3)_5Cl]Cl_2$	24.80	1.73	+14	18.5
78	$[Cr(OH_2)_6]Cl_3$ (blue).....	22.42	1.77	+ 4	18.7
79	$[Cr(OH_2)_4Cl_2]Cl + 2H_2O$ (green) ..	22.60	1.70	+17	18.4

Unfamiliar organic groups may be identified by their names, which are found under "Remarks." Salts Nos. 50, 53, 54, and 64 had partly decomposed, so that they contained more iron than the formulæ indicate. The true molecular weights as determined by iron analyses are shown. It should be noted that the last three salts listed in Table V. are ferrous salts.

None of the salts listed in either table shows any features of any particular interest. To the first order of accuracy the Curie constants and the Weiss magneton numbers are normal, and the values of θ show no larger fluctuations than are found in the simpler salts. One salt that may be noted is the chromi-cyanide $K_3Cr(CN)_6$, No. 73. With Cr are associated 18.5 magnetons, approximately the usual 19 found with simple chromic salts, whereas the corresponding cobalt salt is diamagnetic, and the ferricyanide $K_3Fe(CN)_6$ gives the low magneton numbers 11.9 and 11.2 according to the temperature range.

It may also be noted that the salts $\text{Fe}(\text{ClO}_4)_3(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_6$ No. 61, and $\text{Fe}(\text{CH}_3\text{COCHCOCH}_3)_3$, No. 65, are quite normal according to the present measurements. Magnetron numbers of 50.3 and 32.4, respectively, have recently been reported for these two salts*.

IV. Coordination Compounds of Chromium and Cobalt.

Table VII. and fig. 5 contain the data observed with a series of chromium and cobalt coordination compounds

TABLE VII.
Chromium and Cobalt Coordination Compounds.

Reference No.	SALT.	$K \times 10^6$ (20° C.).	C.	θ .	p .
80	$[\text{Cr}(\text{en})_3](\text{SCN})_3 + \text{H}_2\text{O}$	14.60	1.82	+10	18.9
81	$[\text{Cr}(\text{en})_3]\text{I}_3 + \text{H}_2\text{O}$	9.69	1.79	+13	18.8
82	$[\text{Cr}(\text{en})_3](\text{NO}_3)_3$	14.90	1.79	+15	18.8
83	$[\text{Cr}(\text{en})_3]\text{Cl}_3 + 4\text{H}_2\text{O}$	14.59	1.74	+15	18.5
84	$[\text{Cr}(\text{en})_2(\text{SCN})_2]\text{Br}$ (cis.)	16.18	1.71	+15	18.4
85	$[\text{Cr}(\text{en})_2(\text{SCN})_2]\text{Cl}$ (cis.)	18.15	1.70	+12	18.3
86	$[\text{Cr}(\text{en})_2(\text{SCN})_2]\text{Cl}$ (trans.)	18.15	1.70	+12	18.3
87	$\frac{1}{2}[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6] + \frac{2}{3}\text{H}_2\text{O}$	26.47	1.77	+17	18.7
88	$[\text{Cr}(\text{en})_3][\text{Co}(\text{CN})_6]$	13.38	1.75	+ 9	18.6
89	$[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$	13.64	1.75	+14	18.6
90	$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	16.68	1.78	+ 9	18.8
91	$[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$	16.77	1.75	+15	18.6
92	$[\text{Co}(\text{en})_3][\text{Cr}(\text{C}_2\text{O}_4)_3]$	11.38	1.82	+13	19.0
93	$[\text{Co}(\text{en})_2\text{C}_2\text{O}_4][\text{Cr}(\text{en})(\text{C}_2\text{O}_4)_2]$	11.38	1.85	+ 8	19.1

kindly loaned me by Professor P. Pfeiffer, of Bonn. To avoid superposition and confusion, some lines have been omitted from the figure. These data are of interest chiefly in that they verify, to a first approximation, the results of Rosenbohm †, who measured a very large number of salts of these types at one temperature only. In the main, the present results justify Rosenbohm's assumption of the simple Curie law $K_a T = C$, since θ is in all cases relatively small. Rosenbohm's conclusion that the geometrical and coordination isomers cannot be distinguished by magnetic means is confirmed.

* Berkman & Zoehner, *Zeit. f. Phys. Chem.* cxxiv. p. 318 (1926).

† *Loc. cit.*

V. A Ferricyanide and some Ferric Penta-cyano Derivatives.

The data on this type of ferric salt are shown in Table VIII. and in fig. 6. The ferricyanide was a sample from

Fig. 5.

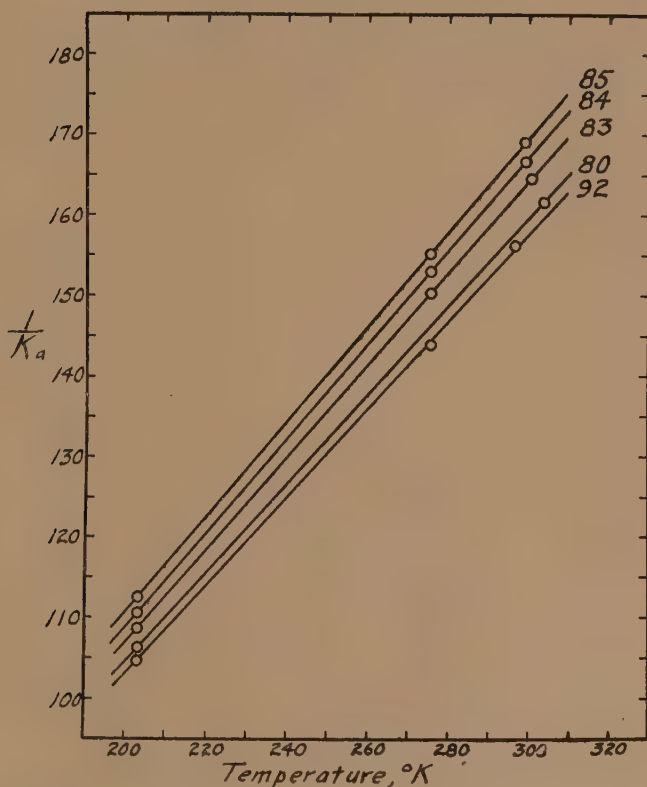
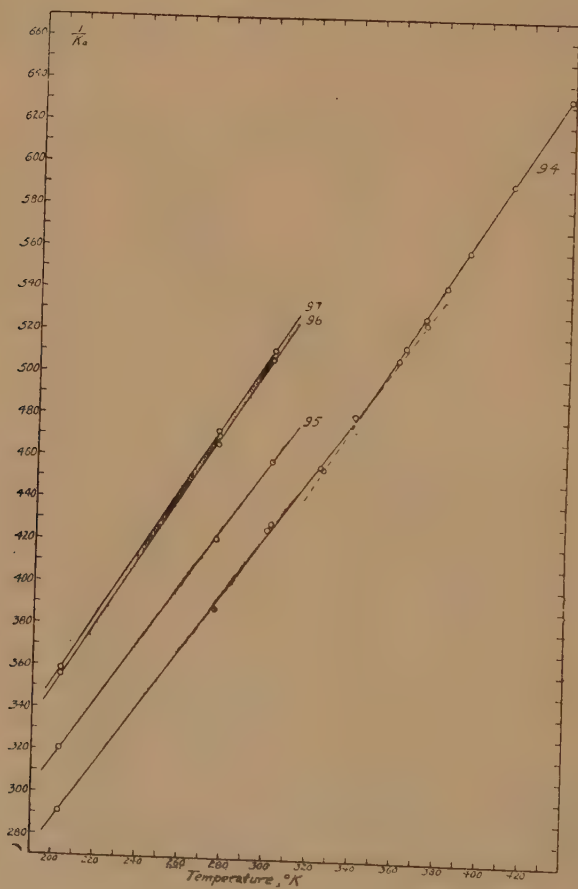


TABLE VIII.—Ferricyanide and Penta-cyano Derivatives.

Reference No.	SALT.	$K \times 10^6$ (20° C.).	C.	θ .	p .	Re- marks.
94	$K_3Fe(CN)_6$	6.97	0.720	— 6	11.9	
	„	...	0.635	+37	11.2	
95	$[Na_2Fe(CN)_5NH_3] + 2H_2O$...	7.43	0.707	—24	11.8	Anal.
96	$[Na_2Fe(CN)_5OH_2] + 2.6H_2O$...	6.38	0.641	—25	11.3	Anal.
97	$[Na_3Fe(CN)_5NO_2] + 2H_2O$..	5.60	0.639	—25	11.2	Anal.

Merck's, and the penta-cyano derivatives were made and analysed by Dr. Davidson at this Institute. These ferricyanide derivatives have been described by Hoffmann*, whose methods of preparation were largely followed in the preparation of the present samples. The main conclusion that

Fig. 6.

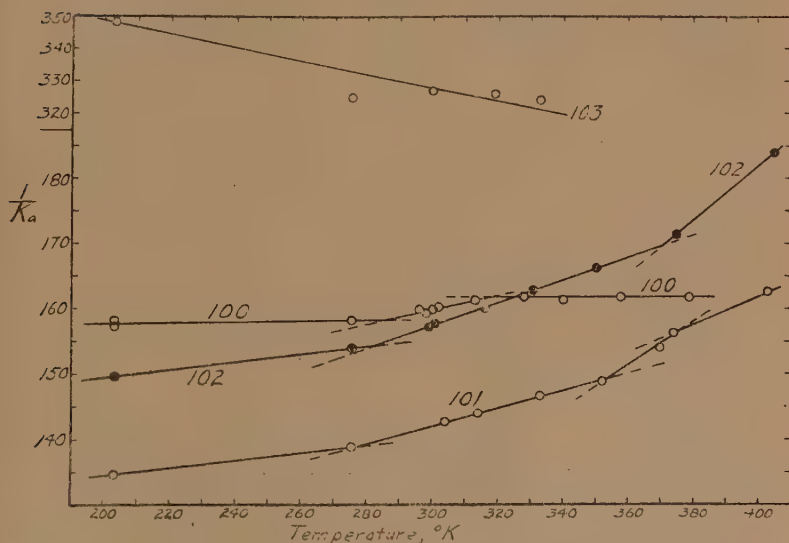


can be drawn from this part of the work is that the low moment found in the ferricyanide is retained without material alteration on substitution of other groups for the CN radicle. The moments observed in the penta-cyano compounds fall

* Hoffmann, *Ann. der Chem.* cccxii. p. 1 (1900).

within the limits 11.2 and 11.9 magnetons observed in $\text{K}_3\text{Fe}(\text{CN})_6$ above and below its transformation point at 62°C . The fact that the amino salt, No. 95, appears with a higher moment than the aquo and nitro salts, Nos. 96 and 97, is not due to experimental errors. Each of them was measured twice, and they gave each time magneton numbers which agreed with the values of the table within 0.2 unit. It seems possible, in view of the two moments observed in the ferricyanide, that a suitable temperature range could be found in which the amino, the aquo, and the nitro salts would have identical moments.

Fig. 7.



Attention may be called to the fact that the specific susceptibilities of the ferric penta-cyano compounds listed in Table VIII. are from 62 to 78 per cent. of the values reported in a preliminary note* three years ago. A part of this discrepancy is due to the better quality of the salts used since. The present measurements were made on the third set of salts that have been prepared at this Institute. But the larger part of the discrepancy arises from my previous use of $\text{K}_3\text{Fe}(\text{CN})_6$ as a standard, and from the fact that I had taken its susceptibility to be $K = +9.0 \times 10^{-6}$. This value

* Welo, 'Nature,' cxvi. p. 359 (1925).

due to Oxley* (corrected for the newer susceptibility of water, $K = -0.719 \times 10^{-6}$) seemed to be supported by those given in the physical tables, which are about 8 or 9×10^6 . At that time I was not aware of Ishiwara's† measurements on $K_3Fe(CN)_6$. His value of K at $21^\circ C.$ is $+7.08 \times 10^{-6}$, which is in as close agreement with $K = +6.97 \times 10^{-6}$, as shown in Table VIII., as can be expected from different samples.

Ishiwara studied $K_3Fe(CN)_6$ throughout a temperature range from $+21^\circ C.$ down to $-148^\circ C.$ When $\frac{1}{K_a}$ is plotted against T , his values fall very accurately on a straight line within the range $-12^\circ C.$ to $-118^\circ C.$ The values of C , θ , and p as determined by this straight line turn out to be 0.925 , -68 , and 13.5 respectively. Accordingly, $K_3Fe(CN)_6$ has still another transformation point at some lower temperature.

The magnetic data on solid $K_3Fe(CN)_6$ herein given are in fairly close agreement with those of Miss Collet‡, obtained with solutions. Her magneton numbers are 11.4 for concentrated solutions and 10.9 for the weak ones. A magneton number of 11 seems strange, in view of the number of the order 29 observed in simple ferric salts. But it may be recalled that the number 11 is associated with iron. We are reminded that the empirical Weiss magneton is, by definition, just one-eleventh of the atomic moment, at saturation, of pure iron.

Incidentally, it may be of interest to mention that $K_3Fe(CN)_6$, the amino salt, No. 95, and the aquo salt, No. 96, yield ferro-magnetic decomposition products on decomposition in air at $300^\circ C.$ The nitro salt, No. 97, was not tried. Qualitatively, these decomposition products behave just like oxidized precipitated magnetite§. The permeabilities are smaller, but of the same order of magnitude as in precipitated magnetite, and on heating to $600^\circ C.$ a non-reversible transformation takes place. Ferromagnetism does not appear on cooling again.

VI. Soluble and Insoluble Prussian Blue.

Soluble and insoluble Prussian blue will be very briefly considered in this paper, since the measurements and their

* Oxley, *Proc. Camb. Phil. Soc.* xvi. p. 107 (1910-1912).

† Ishiwara, *Sci. Rep. Tohoku*, iii. p. 303 (1914).

‡ Collet, *Compt. Rendus*, clxxviii. p. 937 (1924).

§ Welo and Baudisch, *Phil. Mag.* l. p. 399 (1925); Sosman and Posnjak, *J. Wash. Acad. Sci.* xv. p. 329 (1925).

significance to the disputed question of structure are being published elsewhere*.

Soluble Prussian blue is regarded as a potassium-ferric salt of hydro-ferrocyanic acid with the formula $\text{K Fe} [\text{Fe}(\text{CN})_6]$, while insoluble Prussian blue is the ferric salt of the same acid with the formula $\text{Fe}_4 [\text{Fe}(\text{CN})_6]_3$. It is well known that the ferrocyanides are diamagnetic, and we shall see in the last section of this paper that the paramagnetic contribution of the quadrivalent ion $\text{Fe}(\text{CN})_6$, if any, is practically negligible. The measurements on the soluble blue were therefore computed on the assumption that only one of the two iron ions carries the magnetic moment. In the case of the insoluble blue, it was assumed that only four of the seven iron ions contribute to the paramagnetism of the compound. On the bases of these assumptions, it was found that the ferric ions have approximately the normal moments as observed in simple ferric salts. For the soluble blue, $\text{KFe}[\text{Fe}(\text{CN})_6]$, the magnetic constants were: $C=4.05$, $\theta=+22$, $p=28.3$; and for the insoluble blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, they were: $C=3.92$, $\theta=+15$, and $p=27.8$.

VII. Salts showing Anomalous Temperature Variation of $1/\text{K}_a$.

Of all the salts examined during the course of the work, only four were found to show irregularities in the curves $\frac{1}{\text{K}_a} = f(T)$ other than the frequent change of slope indicating a reversible transformation. No. 100 was a triglycolate $[\text{Fe}(\text{OCH}_2\text{COO})_3]\text{H}_3(\text{C}_5\text{H}_5\text{N}) + 2\text{H}_2\text{O}$ with a susceptibility of $+15.4 \times 10^{-6}$ at 20°C . No. 101 was a diglycolate $[\text{Fe}(\text{OCH}_2\text{COO})_2]\text{H}(\text{C}_5\text{H}_5\text{N}) + \frac{1}{2}\text{H}_2\text{O}$ whose susceptibility at 20°C . was $+24.1 \times 10^{-6}$. No. 102 was $[\text{FeF}_4]\text{K}$ with a susceptibility of $+37.3 \times 10^{-6}$ at 20°C . No. 103 was a polynuclear chloracetate of the type considered in the first part of this paper. Its formula was $\frac{1}{3}[\text{Fe}_3(\text{C Cl}_3\text{COO})_6(\text{OH})_3] + \frac{7}{3}\text{H}_2\text{O}$, and its susceptibility at 20°C . was $+6.5 \times 10^{-6}$. The four salts were obtained from Professor Weinland†.

Nos. 100, 101, and 103 were analysed here at the time of the magnetic measurements. The curves obtained are shown in fig. 7. Values of C and p , calculated from the short middle portions of the curves, where they are apparently straight lines, yield values of these magnetic contents larger than the usual values for the ferric ion. The C values for Nos. 100,

* Davidson and Welo, *Journ. Phys. Chem.* (in press).

† *Zeit. anorg. Chem.* cli. p. 271 (1926) and cl. p. 47 (1925).

101, and 102 are, respectively, 9.00, 7.20, and 5.51, leading to the magneton numbers 42, 38, and 33. With No. 103 no computations are possible.

These salts are unstable. It is quite certain that Nos. 101 and 102 contained ferro-magnetic decomposition products before being heated during the measurements. No. 101 became strongly ferromagnetic on being heated in air at 170° C. No. 102 became ferromagnetic on heating at 150° C., and very strongly so after being heated at 300° C. In both cases the decomposition products became simply paramagnetic after having been heated at 600° C. The decomposition products of Nos. 100 and 103, on the other hand, do not go through the ferromagnetic stage, but change directly to a paramagnetic condition which is not altered by heating at 600° C. The presence of a ferro-magnetic impurity in Nos. 101 and 102, due to decomposition, would account for the flatness of the curve $\frac{1}{K_a} = f(T)$ and large values of C and p , since the ferromagnetic part is relatively insensitive to temperature changes. Salts Nos. 100 and 103, which decomposed very rapidly at 75° C., were probably decomposing, during the measurements, into more paramagnetic forms at such rates as to make $\frac{1}{K_a}$ apparently constant in the case of No. 100, and fast enough to make $\frac{1}{K_a}$ decrease in the case of No. 103.

The true magnetic constants are therefore unknown. The glycolates, Nos. 100 and 101, could be diamagnetic for all that the present measurements tell us. It is more probable that the ferric ions carry the normal moments, but that the salts are characterized by large negative values of θ in the Curie-Weiss law. The glycolate groups would be expected to be electric dipoles, and might give rise to the magnetic behaviour observed in the polynuclear salts as described in Section I. of this paper.

A calculation readily shows that if the salt No. 103, $\frac{1}{3}[\text{Fe}_3(\text{CCl}_3\text{COO})_6(\text{OH})_3] + \frac{7}{3}\text{H}_2\text{O}$, is really of the same type as the polynuclear salts described previously, in which were found the usual ionic moment for the ferric ions, θ in the Curie-Weiss relation $K_a(T - \theta) = C$ would have to be at least -1100.

It is interesting to find that an anomalous behaviour in an iron fluoride has been noted before. Ishiware* studied

* *Loc. cit.*

$\text{FeF}_3 + \text{H}_2\text{O}$. It is indicated by him, however, that the chemical formula was a little doubtful. The susceptibility varied very little throughout the temperature range of $-160^\circ \text{C. to } +170^\circ \text{C.}$ Ishiwara's fluoride, $\text{FeF}_3 + \text{H}_2\text{O}$, and the present $[\text{FeF}_4] \text{ K}$ were both, probably, contaminated by a ferromagnetic decomposition product.

TABLE IX.—Diamagnetic and Near-Diamagnetic Salts.

Reference No.	SALT.	No. of Measurements.	$K \times 10^6$.	$K_a \times 10^6$.	Remarks.
104	$\text{H}_4\text{Fe}(\text{CN})_6$	4	-0.328 ± 3	+ 5.0	
105	$\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{H}_2\text{O}$	7	-0.408 ± 2	+ 5.0	
106	$\text{K}_4\text{Fe}(\text{CN})_6$	4	-0.366 ± 1	+ 4.1	
107	$\text{Na}_4\text{Fe}(\text{CN})_6 + 9.5\text{H}_2\text{O}$	4	-0.474 ± 3	- 1.0	Anal.
108	$\text{Na}_4\text{Fe}(\text{CN})_6$	3	-0.340 ± 1	- 2.0	
109	$\text{Ca}_2\text{Fe}(\text{CN})_6 + 10.5\text{H}_2\text{O}$	4	-0.465 ± 1	+ 8.3	Anal.
110	$\text{Na}_3\text{Fe}(\text{CN})_5\text{NH}_3 + 4.2\text{H}_2\text{O}$	3	-0.379 ± 2	+ 18	Anal.
111	$\text{Na}_5\text{Fe}(\text{CN})_5\text{SO}_3 + 8.8\text{H}_2\text{O}$	4	-0.393 ± 6	+ 31	Anal.
112	$\text{Na}_4\text{Fe}(\text{CN})_5\text{NO}_2 + 7.5\text{H}_2\text{O}$	3	-0.364 ± 4	+ 36	Anal.
113	$\text{Na}_3\text{Fe}(\text{CN})_5\text{OH}_2 + 2.3\text{H}_2\text{O}$	4	-0.229 ± 3	+ 52	Anal.
114	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} + 2\text{H}_2\text{O}$	5	-0.348 ± 4	- 4.0	Nitroprusside.
115	$[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{Br}_2$	3	-0.069 ± 1	+ 196	Dipyridyl.
116	$\text{K}_4\text{W}(\text{CN})_8 + 2\text{H}_2\text{O}$	3	-0.365 ± 1	- 27	
117	$\text{K}_4\text{Mo}(\text{CN})_8 + 2\text{H}_2\text{O}$	3	-0.381 ± 1	- 5	
118	$[\text{Co}(\text{en})_2(\text{NH}_3\text{Cl})\text{Br}_2 (\text{lævo})$...	5	-0.305 ± 1	+ 68	
119	$[\text{Co}(\text{en})_2(\text{NH}_3\text{Cl})\text{Br}_2 (\text{dextro})$...	5	-0.292 ± 1	+ 73	
120	$[\text{Co}(\text{en})_2(\text{NH}_3\text{Cl})\text{Cl}_2 (\text{racemic})$...	3	-0.324 ± 1	+ 69	
121	$\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_3$	Est.	+ 0.6	+ 400	Nitrobenzol.
122	K_2CrO_4	Est.	+ 0.04	+ 60	Anal.
123	$\text{K}_2\text{Cr}_2\text{O}_7$	Est.	+ 0.25	+ 60	Anal.
124	CrO_3	Est.	+ 3	+ 300	

VIII. Diamagnetic and Near-Diamagnetic Salts of Various Transition Elements.

The observed specific susceptibilities of these salts and the computed atomic susceptibilities of the metallic ions are tabulated in Table IX. The ferro-cyanides and the nitroprusside were commercial products. The hydro-ferrocyanic acid $\text{H}_4\text{Fe}(\text{CN})_6$ and the penta-cyano compounds were prepared by Dr. Davidson. The cyanides of tungsten and

molybdenum were loaned by Dr. Feldmann, of Hannover, as were the chromates by Dr. Hendricks. The dipyriddy iron salt and the nitrobenzol salt of cobalt are due to Dr. Baudisch and the cobalt amines are due to Dr. King. It is indicated that the susceptibilities of the last four salts were merely estimated. The apparatus used was not sensitive enough for diamagnetic measurements.

The important question with which we become concerned on examining the data of Table IX. is that of "residual paramagnetism independent of the temperature," a conception which it is difficult to reconcile with prevailing magnetic theory. It has been supposed that potassium ferrocyanide $K_4Fe(CN)_6 + 3H_2O$ is one of the compounds in which the metallic ion appears with a small positive residual susceptibility after correction for diamagnetism of the other constituents. $KMnO_4$, K_2CrO_7 , and the cobalt amines are familiar examples.

In view of the present results it is very doubtful if $K_4Fe(CN)_6 + 3H_2O$ belongs in this category. The best indication that it does not is the fact that the corresponding sodium salts Nos. 107 and 108 give residuals which are definitely not positive. Other points in the evidence against residual para-magnetism in iron in the ion $[Fe(CN)_6]$ are as follows :—

1. $H_4Fe(CN)_6$ apparently has a residual atomic susceptibility of $+5 \times 10^{-6}$, but it is known that the diamagnetic susceptibility of this acid is really more than -0.328×10^{-6} . The acid decomposes at ordinary temperature into the paramagnetic Prussian blue. The particular sample used, which gave $K = -0.328 \times 10^{-6}$ soon after preparation, was found, 22 months later, to be actually paramagnetic. Hence $K = -0.328 \times 10^{-6}$ is certainly too small, and does not represent the true diamagnetic susceptibility. An increase in K by 7.5 per cent. to $K = -0.352 \times 10^{-6}$ would remove the apparent positive residual of $+5 \times 10^{-6}$ for iron in $H_4Fe(CN)_6$.

2. The evidence is that the susceptibility of potassium ferrocyanide depends on the field strength. The present susceptibility of $K = -0.408 \times 10^{-6}$ was obtained with a field intensity of 11,000 gauss. This is in substantial agreement with Oxley*, who, however, does not state the

* *Loc. cit.*

field intensity. Ishiwara * used field strengths of about 2600 gauss, and found $K = -0.352 \times 10^{-6}$, which leads to a positive atomic susceptibility for iron of $+29 \times 10^{-6}$ as compared with about $+5 \times 10^{-6}$ in the present experiments. These distinct susceptibility values at different fields indicate the presence of a trace of ferromagnetic material.

3. The ferromagnetic traces suspected to be present in the ferrocyanides are the natural decomposition products. All of the ferrocyanides, the penta-cyano compounds and the nitro-prusside listed in Table IX. (the dipyriddy salt No. 115 was not tried), yield ferromagnetic decomposition products on being heated in air at 300°C . On heating to 600°C ., a non-reversible transformation takes place, and they become merely paramagnetic.

In connexion with the ferrocyanides, it is to be observed that the potassium and sodium salts were also measured in the dehydrated condition brought about by heating to constant weight in an atmosphere of nitrogen at 125°C . This was done, not so much to test for a direct magnetic effect of the water of crystallization, as to decide on the diamagnetic correction to apply for water. The correction as calculated from Pascal's additive law is -10.4×10^{-6} , whereas the observed molecular susceptibility for water is $-0.719 \times 10^{-6} \times 18 = -13 \times 10^{-6}$. Use of the latter value in computing K_a for hydrated potassium and sodium ferrocyanides leads to values of K_a which agree, within one unit, with the values of K_a found for the dehydrated salts. As an incidental matter, the conclusion is justified that water, as water of crystallization, is magnetically identical with water in the liquid state.

The ferrous penta-cyano compounds, although diamagnetic, yield positive residuals for iron which are larger than the residuals shown by the ferrocyanides. As has been pointed out, these salts give ferro-magnetic decomposition products, so that the observed diamagnetic susceptibilities are likely to be too low. It would be interesting to study these ferrous penta-cyano compounds over a range of low temperatures to see if there is present, also, a trace of the corresponding ferric salt which, as has been seen in Section V., is paramagnetic. Ishiwara has already shown that $\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{H}_2\text{O}$ is free from any paramagnetic component, since the susceptibility was constant between room and liquid air temperatures.

* *Loc. cit.*

It is to be observed that the ferrous aquo salt No. 113, $\text{Na}_3\text{Fe}(\text{CN})_5\text{OH}_2$, falls into line with the other ferrous penta-cyano salts, in contrast to my previous results as presented in a letter to 'Nature'*. At that time it was thought to be paramagnetic and to approach in strength the ferric penta-cyano salts. This salt is especially likely to oxidize to the paramagnetic ferric form unless great precautions are taken.

The nitro-prusside, No. 114, is the only ferric penta-cyano compound so far known to be diamagnetic. It also yields a negative susceptibility for the iron in it. One is tempted to regard diamagnetism in this salt as being due to compensation of the moment associated with the ferric ion by that of the NO group. Quantitatively, however, there arises a discrepancy of 2 Weiss units, since the moment of the NO molecules is 9 magnetons.

No importance is to be attached to the susceptibility value and the positive residual found for the dipyriddy compound $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{Br}_2$. Only one sample was available, and the quantity was too small to permit accurate measurements. It is included in the table merely as an additional example of a salt which is diamagnetic in spite of the presence of iron. The corresponding sulphate (instead of bromide) has been reported as diamagnetic by Berkman and Zocher†, but it is difficult to accept their value for the susceptibility, $K = -1.7 \times 10^{-6}$.

The cobalt amines containing the ethylene-diamine groups ($\text{en} = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) are diamagnetic, as Rosenbohm found them to be, but the mean value of the atomic susceptibility for the cobalt, $K_a = +70 \times 10^{-6}$, is a little higher than his value of $K_a = +60 \times 10^{-6}$. The lack of agreement seems to be outside of the experimental error. The samples were old, having been prepared in 1911. These salts do not yield ferromagnetic decomposition products, but they become paramagnetic on heating for a few minutes at 350°C . The presence of a small trace of a paramagnetic component is suggested by an observation on the salt $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, of the same lot as the cobalt amines and, presumably, prepared at about the same time. According to Rosenbohm, this salt should be diamagnetic. It was paramagnetic with $K = +11.3 \times 10^{-6}$.

The two chromates, Nos. 122 and 123, are seen to give positive residuals for chromium in close agreement with the

* *Loc. cit.*

† *Loc. cit.*

value $K_a = +63.3 \times 10^{-6}$ found by Weiss and Collet* in the dichromate $K_2Cr_2O_7$.

The value $K = +3 \times 10^{-6}$ for CrO_3 is too high on account of partial decomposition. For this substance Ishiwara found an initial susceptibility $K = +0.51 \times 10^{-6}$, and that the susceptibility rose to very high values on heating. On still further heating, CrO_3 became Cr_2O_3 and less magnetic with $K = 28.5 \times 10^{-6}$.

In conclusion, it may be remarked that salts such as the cobalt amines and the chromates, which seem to yield small positive residuals for the susceptibilities of the metals, need very careful studies as to the constancy of the susceptibilities when the temperature is varied. Miss Collett in collaboration with Weiss has studied a luteo cobalt salt and $K_2Cr_2O_7$, both as solids and in solution. The detailed results have not been given, as far as I know, but the published note gives the impression that the susceptibilities are constant only within very narrow limits. One element of difficulty in this problem of residual paramagnetism independent of the temperature is, of course, that of the proper diamagnetic constants to be used for correction. An equally difficult one is that of excluding or allowing for possible paramagnetic components.

It is a pleasure for me to express my thanks to those who have supplied me with material and who have, in other ways, contributed towards this work. I am especially grateful to Professor R. Weinland, Professor P. Pfeiffer, and Dr. D. Davidson for supplying so many salts of uniformly high quality. Dr. S. B. Hendricks, Dr. K. Feldmann, and Dr. V. King have also contributed many rare salts. Dr. O. Baudisch was largely instrumental in obtaining the material from abroad, and it is to him that I owe my interest in the subject of complex salts. Thanks are due to the General Electric Company for their kindness in lending the electromagnet.

Rockefeller Institute for Medical Research,
New York, April 12th, 1928.

* Weiss & Collet, *Compt. Rend.* clxxviii. p. 2146 (1924), clxxxi. p. 1057 (1925).

L. *The Surface Tension of Liquid Metals.*—Part III. *The Surface Tension of Mercury.* By L. L. BIRCUMSHAW, M.A., M.Sc.*

THE surface tension of mercury has been the subject of many investigations under very different conditions and by many different methods. The more recent work may be briefly reviewed. Stöckle† formed a drop of mercury in an enclosed vessel which could be evacuated or filled with a pure dry gas. Treating the surface of the drop as a convex mirror, he determined the position of an object and its image, from which the radius of curvature at the vertex was calculated. He obtained some very remarkable results, which are given in Table I.

TABLE I.

Gas.	t° .	Initial γ . mg./mm.	γ (after 1 hour). mg./mm.
Vacuum	15	44.4	44.4
Hydrogen	21	47.9	44.2
Air (dry)	17	48.5	43.7
Air (moist)	17	49.4	43.7
Carbon dioxide	19	49.0	44.4
Oxygen	23	48.7	44.0
Nitrogen	16	49.8	44.6

It was found that if a determination was made as rapidly as possible (in a few seconds) *in vacuo*, the value 44.4 mg./mm. was obtained, and this value was unchanged in one hour's time. If the drop were formed, however, in a gas, the initial value was much higher, but fell after a time to the value obtained *in vacuo*. Stöckle determined the fall of surface tension with time, and gives curves for all the above gases. It was found that the initial high values fell very rapidly in hydrogen (about 5 minutes), more slowly in carbon dioxide, and still more slowly in nitrogen, which required about fifty minutes for the value to fall to that obtained in a vacuum. He considered the effect to be due to the condensation of gas on the surface of the mercury. Stöckle's results are in general confirmed by

* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

† *Ann. d. Physik*, lxvi. p. 499 (1898).

Meyer*, who used the vibrating jet method, and therefore found higher initial values (51.5 mg./mm. in air and 56.5 in hydrogen).

Kalähne† formed stationary waves by means of the interference of two progressive circular wave systems in the surface of some mercury, and produced in this way what is, in effect, a plane reflexion grating. The wavelength of these small ripples is then equal to the constant of the grating, and this was measured, using sodium light. He obtained rather lower values than Stöckle, his highest being 44.0 mg./mm. at 18°.

Cenac‡ measured the surface tension of mercury in air and a vacuum at 0°, and found 437 dynes/cm. in air and 460 *in vacuo*. He used the drop-weight method and Lohnstein's corrections. A more recent determination by the same method by Harkins§ gave 476 dynes/cm. *in vacuo* and 465 in air.

Hogness|| found no difference in the surface tension of mercury in hydrogen when the pressure of the gas varied from 300 mm. down to a vacuum giving the green fluorescence of the glass with the electric discharge. No difference was detected when hydrogen was replaced by dry air.

Iredale¶, by means of the drop-weight method and mercury distilled into the apparatus *in vacuo*, obtained 456 dynes/cm. at 18–19° in air at atmospheric pressure (approx.), and as the pressure was decreased, the surface tension diminished to 410 dynes/cm. at 10^{-4} mm. Iredale suggests that there is some impurity present which lowers the surface tension, and this impurity is more effective in a vacuum. Removal of the taps in the apparatus, with their attendant lubricant, had no effect, however. In further experiments mercury was re-distilled twice in a current of air and then *in vacuo*. After distilling the metal into the apparatus, determinations were made as quickly as possible, and a value of 475 dynes/cm. was obtained at a pressure of 10^{-5} mm. On admitting air the value fell to about 460 dynes/cm., and after re-evacuating it fell to 410 dynes/cm. Experiments made with water-vapour in the dropping chamber gave a value of 411 dynes/cm., which is almost the same as that found for mercury *in vacuo*; the

* *Ann. d. Physik*, lxvi. p. 523 (1898).

† *Ann. d. Physik*, vii. p. 440 (1902).

‡ *Ann. Chem. et Phys.* p. 299 (1913).

§ *J. Amer. Chem. Soc.* xlii. p. 2539 (1920).

|| *J. Amer. Chem. Soc.* xliii. p. 1621 (1921).

¶ *Phil. Mag.* xlviii. p. 177 (1924).

suggestion is made that the adsorption of water-vapour from the glass is the cause of some of the anomalous results obtained. A further suggestion made by Iredale in this paper is that the pressure of air may raise the pressure of water-vapour necessary to form an adsorbed film.

In a further communication * Iredale has determined the surface tension of mercury by the measurement of a sessile drop. The mercury is distilled on to a glass plate enclosed in a glass chamber which can be evacuated. He uses the simple formula :

$$h^2 = a^2 = \frac{2\gamma}{\rho g},$$

where h is the distance from the maximum diameter of the drop to its vertex. Drops of about 1.5 cm. in diameter are employed. He found that the first few drops distilled over gave a low value, but that this rose after successive quantities were distilled, and he suggests that the first portions of the mercury tend to remove some impurity from the glass surface. From a measurement of eleven successive drops the surface tension rose from 430 to 465 dynes/cm., and after remaining for 24 hours *in vacuo* the value was found to be 446 dynes/cm. The admission of pure dry air to a mercury surface formed *in vacuo* does not alter its surface tension to any great degree, but unpurified air appears to lower it considerably, and the contamination is irreversible. Iredale considers that "when a surface is formed in air at atmospheric pressure the presence of the air may hinder the adsorption of the impurities, but the admission of air to a surface already formed in a vacuum does not appear to result in a de-sorption of impurities."

Popesco † has determined the surface tension of mercury by the previous method, and found a value of 436 dynes/cm. when the drop is formed and kept in a vacuum. If the drop formed *in vacuo* is exposed to a gas a decrease in the surface tension is observed. When a surface is formed in a gas the initial surface tension is greater than when formed *in vacuo*, but decreases after a time to the vacuum value. Popesco investigated these effects with different gases and at different pressures. It will be seen that he confirms in general Stöckle's results, and he ascribes these effects partly to adsorption and partly to the orientation of molecules in the liquid. Langmuir has shown that the initial velocity of

* Phil. Mag. xlix. p. 603 (1925).

† Ann. de Physique, iii. p. 402 (1925).

photo-electrons emitted from a mercury surface is modified similarly when the drop formed *in vacuo* is exposed to a gas. Popesco confirms this and points out the close parallelism between this phenomenon and surface tension.

Sauerwald and Drath* have recently made some determinations of the surface tension of mercury by the bubble-pressure method. These authors made experiments with a thick-walled glass capillary (0.61–1.28 mm.), a thin-walled glass capillary (0.035–0.05 mm.), and a thin-walled etched glass capillary. Their results are as follows ($t=19^\circ$):—

	γ .
Thick-walled capillary	465–480 dynes/cm.
Thin-walled capillary	453–476 „
Thin-walled capillary etched	465–474 „

A specially selected capillary with a thick wall gave results which varied from 469–479.8 dynes/cm., and a thin-walled etched silica capillary gave values from 469–477.5 dynes/cm. The influence of the depth to which the tube dipped in the metal was also investigated, and it was found that constant results were obtained when this exceeded 3 mm.

Burdon and Oliphant†, by the photography and measurement of a sessile drop, have repeated Popesco's work and confirmed his conclusions. They also found by means of the drop-weight method that mercury gives values when the drop is formed in air, which are only 1 per cent. higher than when the drop is formed *in vacuo*, and they consider that the drop-weight method fails to detect the differences between the air and vacuum values. They criticize the drop-weight method on the grounds that it is finally based on the value for the surface tension of water obtained by the method of capillary rise in glass tubes, and that the method has been based on determinations made with liquids of approximately unit density which are suspended from the outer circumference of a tube. They are doubtful as to whether the form of drop will be the same for liquids of high density, *e.g.* mercury which hangs from the inner circumference.

In view of the considerable divergence of the results found by previous workers, it was considered of interest to investigate the surface tension of mercury by means of the

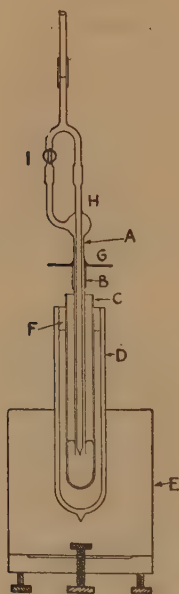
* *Zeit. Anorg. Chem.* cliv. p. 79 (1926).

† *Trans. Farad. Soc.* xxiii. p. 205 (1927).

maximum bubble pressure method under a number of different conditions, viz. :—

- (a) The use of tubes constructed of glass (soft).
- (b) The use of tubes constructed of silica.
- (c) The use of different gases for blowing the bubbles.
- (d) Varying the time of formation of the bubbles.
- (e) Different physical conditions of the surface of the ends of the tubes.

Fig. 1.



Experimental.

The apparatus is shown in fig. 1. It consists of an outer tube A 30 cm. long which fits tightly through the collar B. This collar carries a plate G, and through the top of the outer tube at H is fused a tube of smaller diameter which is drawn out to a capillary at its lower end. The ends of both tubes are ground carefully so that the cross-section of each is in the same plane, and this plane is parallel to the surface of the plate. The mercury is placed in the container * C,

* The glass container used had an internal diameter of 3.0 cm., and the internal diameter of the silica container was 2.7 cm.

which fits by means of a thick pad of cotton-wool F into a thermos flask D, which in turn is supported by a large wooden block E. The tubes are suspended in the mercury from a bracket attached to the plate, and this bracket is held by a heavy rigid iron stand. The stand, at its base, is supported on three levelling screws. By manipulating these the plate can be levelled up, when the ends of the tubes will be in a horizontal plane in the liquid. By closing or opening the tap I bubbles can be blown at will from the narrow or the wide tube. The procedure was, of course, the same as in the previous work*, viz. the difference in pressure required to detach a bubble, first from the wide and then the narrow tube, was measured. All the measurements were made at 20° C. The mercury in the container was placed in a thermostat for 15 minutes and rapidly transferred to the thermos flask. If the temperature of the room were kept at about 20°, then the temperature of the mercury, after a series of measurements had been made, was rarely found to have altered by more than 0.5°.

The mercury† was purified in the following manner:—A quantity of the metal was placed in a porcelain dish and floated on the surface of some mercury contained in a much larger dish. The whole was then covered with water containing a little sulphuric and nitric acids and electrolysed, using platinum wire electrodes with a current of 0.5 amp. for twenty-four hours. The mercury in the larger dish, which was the anode chamber, was then removed and dried. It was then distilled in air and finally in another still at a pressure of about 10 mm. of air.

The gases used were purified in the following manner:—

Hydrogen (generated electrolytically from caustic soda solution using an iron cathode) was dried, and passed through a silica tube at 600° to free the gas from traces of oxygen. It was then passed through a series of calcium-chloride tubes. Nitrogen was taken from a cylinder and passed over copper gauze heated to 600°, and a short length of iron gauze heated to 800°. The iron gauze had been previously oxidized and then reduced in hydrogen. The gas was then dried by passage over calcium chloride. Oxygen was taken from a cylinder and dried. Carbon dioxide was prepared from marble and hydrochloric acid; the gas passed through sodium-bicarbonate solution and dried through calcium-chloride tubes. In the actual determinations all these gases, with the exception of the carbon

* Phil. Mag. ii. p. 341 (1926).

† For the preparation of the mercury I am indebted to Mr. S. Watts.

dioxide, were finally (before entering the apparatus) passed through a tube immersed in solid carbon dioxide and acetone to remove the last traces of water. When carbon dioxide (gas) was used the final drying agent was phosphorus pentoxide.

In the first apparatus used the tubes (glass) had the following mean dimensions:—

External diameter of outer tube	1.156 cm.
Internal diameter of outer tube	1.009 „
External diameter of inner tube	0.0964 „

Perfectly concordant results were obtained with this apparatus, which gave:—

P wide.	P (narrow).	a^2 .	γ dynes/cm.
22.5	35.35	0.07477	497

The pressures are given in cms. of water. Experiments were then made to determine how the surface tension varied when the bubble was held on the end of the inner tube, at a pressure just below that at which it becomes detached, for various lengths of time. Normally about 40–50 secs. was taken to form and detach the bubble, and in these experiments the pressure in the bubble was developed to a value 3–5 mm. below that at which it was normally detached, held for various times, and in each case the final pressure at which the bubble was liberated was read. After each of these determinations the normal pressure (*i.e.* the reading obtained in the ordinary way in 40–50 secs.) was determined, and this practically never differed from the initial ordinary reading. It was found that the lowering of the pressure at which the bubble was detached always increased as the time the bubble was held on the end of the tube increased, but that the magnitude of the effect was hardly ever the same in experiments made on two consecutive days.

A large number of experiments were made and two series are given in Table II. The two series give (1) the smallest lowering obtained and (2) the highest.

TABLE II.

(1.)

Time (mins.).	P wide.	P narrow.	a^2 .	γ dynes/cm.
0	22.5	35.35	0.07477	497
5	22.5	35.25	0.07438	494
10	22.5	35.15	0.07399	492
15	22.5	34.95	0.07320	489
30	22.5	34.95	0.07320	489
60	22.5	34.7	0.07222	480

(2.)

Time (mins.).	P wide.	P narrow.	a^2 .	γ dynes/cm.
0	22.4	35.15	0.07419	493
10	22.4	34.8	0.07278	483
20	22.4	34.5	0.07152	475
30	22.4	34.4	0.07111	472
45	22.4	34.0	0.06947	461

The surface of the ends of the tubes in this apparatus was distinctly roughened. It had been ground with No. 3 emery. The ends were carefully polished with fine emery. On measurement the diameter of the inner tube was found to be 0.0982 cm. and the dimensions of the outer tube the same as before. The apparatus then gave the following:—

P wide.	P narrow.	a^2 .	γ dynes/cm.
22.05	34.8	0.07569	502

This result could be repeated to less than 0.5 per cent. (0.05 cm. in the pressure difference) any number of times.

A similar apparatus was constructed with silica tubes instead of glass. They had the following dimensions:—

Mean external diameter of outer tube ...	0.923 cm.
Mean internal diameter of outer tube ...	0.760 „
Mean external diameter of inner tube ...	0.1022 „

The ends of these tubes were carefully polished. Various values were obtained with this apparatus, four of which are as follows:—

P wide.	P narrow.	a^2 .	γ dynes/cm.
20.8	39.8		
20.8 (a)	39.4 (a)	0.10136	673
20.8	39.5		
20.8	39.8		

The result of one of these readings (a) has been calculated. The tubes were then etched for ten minutes in dilute hydrofluoric acid, when the diameter of the inner tube was found to be 0.1004 cm. Very high values were again obtained, as will be seen from the following readings, which also differ considerably among themselves:—

P wide.	P narrow.
21.2	36.6
21.2	37.7
21.2	36.8
21.2	36.5
21.2	36.6
21.2	36.9
21.2	37.8
21.2	38.0

The ends of the tubes were then roughened by grinding with No. 3 emery. The external diameter of the inner tube was then 0.0998 cm., and the following result was obtained :—

P wide.	P narrow.	a^2	γ dynes/cm.
22.1	34.65	0.07250	481

This result could be repeated any number of times. Experiments were then made holding the bubble on the end of the tube for various times, but practically no difference from the normal could be detected in the pressure required to liberate the bubble. These results are given below :—

Time (mins.).	P wide.	P narrow.	a^2 .	γ dynes/cm.
0	22.1	34.65	0.07250	481
15	22.1	34.60	0.07236	479
20	22.05	34.70	0.07307	485
30	22.05	34.6	0.07250	481

The glass apparatus used in the above work was unfortunately broken. A new one was constructed which had the following dimensions :—

Mean external diameter of outer tube...	1.007 cm.
Mean internal diameter of outer tube...	0.830 "
Mean external diameter of inner tube...	0.0990 "

The figures given by this tube (repeatable to 0.05 cm. in the pressure difference) were :—

P wide.	P narrow.	a^2 .	γ dynes/cm.
22.3	34.95	0.07451	495

This apparatus, unlike the first one used, gave practically no decrease in the reading when the bubble was held on the tube, as the following results show :—

Time (mins.).	P wide.	P narrow.	a^2 .	γ dynes/cm.
0	22.3	34.95	0.07451	495
5	22.3	34.95	0.07451	495
15	22.3	34.90	0.07420	493
30	22.3	34.90	0.07420	493

All the above determinations were made with hydrogen purified as described. Oxygen was next used. A very large number of determinations were made, but it was found to be impossible to obtain concordant readings, and most of these were very high. In some cases the normal reading was obtained a few minutes after placing the tube in the mercury, but the value rose rapidly after a short time. A

typical experiment is detailed below, the initial reading being taken ten minutes after the tubes were placed in the mercury.

Time.	P wide.	P narrow.	a^2 .	γ dynes/cm.
1.0 P.M.	22.25	34.85	0.07486	493
2.15 "	22.25	35.4		
	22.25	35.2		
	22.25	35.9		
	22.25	35.3		
3.0 "	22.15	36.1		
	22.15	36.1		
	22.15	35.8		
	22.15	35.8		
	22.15	35.9		
4.0 "	22.15	35.8		
	22.15	35.75		
	22.15	35.7		
	22.15	35.75		
	22.15	35.7		
5.15 "	22.15	36.5	0.08192	544
	22.15	36.35		
	22.15	36.35		
	22.15	36.35		
	22.15	36.35		

The results obtained with this apparatus when using nitrogen and carbon dioxide, and the readings obtained when the bubble was held on the end of the tube for various times, are given in Table III.

TABLE III.

Nitrogen.

Time (mins.).	P wide.	P narrow.	a^2 .	γ dynes/cm.
0	22.1	34.85	0.07511	499
5	22.1	34.85	0.07511	499
15	22.1	34.85	0.07511	499
30	22.1	34.85	0.07511	499

Carbon Dioxide.

0	22.3	35.0	0.07480	497
15	22.3	34.8	0.07391	491
30	22.3	34.6	0.07301	485

When the bubbles were blown with moist hydrogen (hydrogen passed through water at 20°) the following result was obtained :—

P wide.	P narrow.	a^2 .	γ dynes/cm.
20.3	33.5	0.07611	505

The same result was obtained if a visible covering of water was placed on the mercury in the container.

With the silica tubes the values given in Table IV. were found:—

TABLE IV.

Nitrogen.

Time (mins.).	P wide.	P narrow.	a^2 .	γ dynes/cm.
0	22.1	34.75	0.07288	484
15	22.1	34.75	0.07288	484
30	22.1	34.80	0.07310	486

Carbon Dioxide.

0	21.95	34.5	0.07235	481
15	21.95	34.45	0.07202	479
30	21.95	34.4	0.07173	477

Oxygen.

0	22.5	34.8	0.07161	475
15	22.5	34.8	0.07161	475
30	22.5	34.8	0.07161	475

It will be seen that no appreciable decrease in the readings occurs when the bubbles are held on the end of the tube for as long as 30 minutes.

It was found that the time taken in the development of the maximum pressure of the bubble had no influence on the value obtained when the time was varied between 35 secs. and 2 mins. 30 secs. Variation within wide limits of the depth to which the tubes were immersed in the metal was also found to be without effect on the value.

The chief experimental results are given below in tabular form:—

	Hydrogen.	Nitrogen.	Carbon Dioxide.	Oxygen.
<i>1st glass tube.</i>				
Polished	502			
Roughened	495			
Bubble held 45 mins.....	461			
<i>2nd glass tube.</i>				
Roughened	495	499	497	No results.
Bubble held 30 mins.....	493	499	485	„
<i>Silica tube.</i>				
Polished	673			
Roughened	481	484	481	475
Bubble held 30 mins.....	481	486	477	475

Discussion.

Stöckle's experiments, which appear to have been carried out with great care, are very difficult to explain. It is easy to see, of course, that the presence of a gas might progressively lower the surface tension of a mercury surface, due to the time taken for the adsorbed gas film to reach equilibrium, but it is very difficult to imagine why different gases should reduce the value to that given *in vacuo*. It would have been expected that the initial (rapidly taken) value obtained in a gas would have approached that obtained in a vacuum, after which the surface tension would have diminished to some final equilibrium value. Nevertheless, it is extremely probable that the phenomena observed by Stöckle are genuine, as his results have been, in general, confirmed by Popesco and Burdon & Oliphant. They have been, however, chiefly noticed by workers who have used the "drop measurement" method. Harkins, Hogness, Cenac, and Burdon & Oliphant have found only small differences in the surface tension of mercury in air, and *in vacuo* when measured by the drop-weight method. This may be due to some extent to the relatively long time taken for the drops to form. An interesting explanation of Stöckle's results was first put forward by Bancroft ('Applied Colloid Chemistry,' 1921, p. 134). If we consider mercury to be a partially polymerized liquid, then the molecular modification which has the lowest surface tension will tend to be positively adsorbed at the surface, and equilibrium will be reached when a certain relation exists between the concentration of this modification in the surface layer and in the bulk of the liquid. The attainment of this equilibrium may take a definite time, and Bancroft suggests that it may be instantaneous when a mercury surface is formed *in vacuo*, but relatively slow in the presence of gases. Iredale, as previously stated, considers this lowering to be due to dirt or alkaline material derived from the glass which is much more rapid *in vacuo*. He also considers the possibility of moisture being the cause.

With regard to the results obtained in the present work, the following points call for special comment. It will be seen that distinctly higher results are obtained with glass tubes than with silica. This was found with both sets of glass tubes used, and the results obtained with these agree to less than 0.5 per cent. This value, nevertheless, is distinctly higher than that found by most workers on this subject. Sauerwald and Drath failed to detect any appreciable difference between glass and silica tubes, but the

highest value, 480 dynes/cm., obtained was with glass. A further interesting point is that with glass the same result is obtained whether the end (tip) of the tube is polished or roughened. In the case of the first glass apparatus the fall in surface tension noticed in holding the bubble on the end of the narrow tube was very variable, and in the second apparatus this effect was found to be almost absent. The only obvious explanation for these decreases is that they are due to traces of alkaline material (or dirt) left on the tube in spite of the cleaning treatment*. In view of the fact that they were only obtained with the first apparatus, the cause is more likely to be the specific nature of the glass, but this also may actually be due to surface alkali. The first glass tube was of pre-war German material, but the second was English soft alkali glass. When the bubbles were blown with nitrogen, a result was obtained which was practically identical with that recorded with hydrogen. No decreases on holding the bubble on the end of the tube were observed. When carbon dioxide was used the same normal result was obtained, but small decreases were found when the bubble was held on the end of the tube. With moist hydrogen a slightly higher value was obtained. This may be due to the fact that in this case the bubble does not form on the extreme circumference of the tube. It was also considered possible that, in the presence of so much moisture, the bubble actually formed on the inner circumference of the tube, the surface tension measured being the interfacial tension of mercury-water. Calculated on the inner radius, the figure 314 dynes/cm. was obtained, but the interfacial tension mercury-water, as determined by Harkins, is 375 dynes/cm., so that the above explanation appears to be unlikely.

With the apparatus made of silica the normal value obtained was, as previously stated, lower than that given by the glass apparatus. It is significant that with silica practically no decreases were observed on hanging the bubble on

* Before using the apparatus, the tubes were allowed to stand all night in a mixture of sulphuric and chromic acids, the acid mixture being drawn up into both tubes as far as the top of the bulb. The acid was then removed, the apparatus washed with freshly-distilled water, and then with acetone. The tubes were then inserted through the neck of a flask containing a small quantity of acetone. The latter was boiled and the lower parts of the tube were washed with condensed acetone. This treatment corresponds to "steaming," acetone being used instead of water. The tubes were then surrounded by a clean dry pyrex tube, and dry gas passed through first the inner and then the outer tube for at least two hours.

the end of the tube for a time as long as thirty minutes. This was found to be the case with all the gases used. Another interesting observation is that concordant normal values could not be obtained until the end of the tube had been roughened. This was established by a large number of experiments. Etching the tube with dilute hydrofluoric acid had little influence on the high readings obtained with the polished tubes, and observations of the surface under the microscope after etching showed that it was still very fine grained.

Curious results were obtained when oxygen was used for blowing the bubbles. With the glass apparatus sometimes correct readings were obtained immediately after placing the tubes in the mercury, but after a short time these readings were much too high. Moreover, the correct readings could not always be obtained in the early stages. With a silica apparatus this phenomenon was not observed. It was thought at first that these high values might be due to an oxide film produced on the surface of the tip of the tube which would cause the bubble to be formed nearer the inner circumference, or, of course, the high readings might have been due to real alteration in the surface tension of the mercury. In view of the fact that these observations were not repeated with a silica tube, however, this explanation appears improbable.

It appears from these experiments that values are obtained by the maximum bubble-pressure method for the surface tension of mercury which vary within small limits with the nature of the tube material. In the case of a silica tube the results also vary considerably with the physical condition of the end of the tube on which the bubble is formed. The use of different gases for blowing the bubbles does not appear to affect the results obtained.

The actual mechanism involved in the explanation put forward by Bancroft to explain Stöckle's results is, of course, very obscure. By making certain assumptions, however, it is possible to obtain a relation between the time required to reach equilibrium and the density of the gas.

The energy interchange between the liquid and the gas can only take place during a collision between gas and liquid molecules, so that if

k = the average loss (or gain) of kinetic energy of a gas molecule during a collision with a mercury molecule, and N = number of collisions per second per sq. cm. of surface, then the rate of communication of energy between

the gas and the liquid is equal to kN . If k is assumed to be equal $1/n$ th of the average kinetic energy of a gas molecule, then $kN = 1/n \left(\frac{1}{2} m \bar{v}^2 \right) N$, which is a quantity depending only on the condition of the gas and not on the time required to attain equilibrium at the surface. Therefore

$$kN = \frac{dE}{dT} = \frac{1}{n} \left(\frac{1}{2} m \bar{v}^2 \right) N,$$

$$\text{or} \quad E = \frac{1}{n} \left(\frac{1}{2} m \bar{v}^2 \right) NT,$$

where E is the energy in time T . E is the energy which is transferred to, or from, the liquid in the time required for the surface tension to change from the initial to the final value, and these two tensions presumably correspond with the dynamic and static surface tensions. E will therefore be a constant, and we have,

$$T = \frac{E}{\frac{1}{n} \left(\frac{1}{2} m \bar{v}^2 \right) N} \quad \text{or}^* \quad T \propto \frac{A}{m \bar{v}^3}.$$

Remembering that for any number of gases at the same temperature and pressure

$$m \bar{v}^2 = \text{a constant } c$$

$$\text{and} \quad \bar{v} = cm^{-\frac{1}{2}},$$

$$\text{it is seen that} \quad T \propto m^{\frac{3}{2}};$$

i. e., the time taken to reach equilibrium will be proportional to the square root of the density of the gas.

Stöckle found that the time required to reach equilibrium was much longer in nitrogen and carbon dioxide than in hydrogen. Popesco's figures for the surface tension, 5 seconds, 10 seconds, and 20 minutes after the formation of the drop, are given in the following table:—

	O ₂ .	N ₂ .	H ₂ .	CO ₂ .	SO ₂ .	NH ₃ .
5 secs.....	525	540	510	519	477	476
10 secs.....	505	524	477	509	438	450
20 mins.	438	447	445	455	—	448

Popesco's curves show a rapid fall of surface tension in the first twenty minutes, but from this time to 1 hour the fall is relatively gradual.

It is, of course, possible that the assumptions made in the above argument are unjustified, but, if not, the proportionality between the time for the surface tension to fall to the

* Ignoring variations in the value of n for different gases.

vacuum value and the density of the gas in which the mercury surface is produced do not appear to be in agreement with Popesco's results.

The remarkable phenomena observed by Stöckle and by Popesco cannot be considered to have been explained satisfactorily. The most interesting feature is that they appear to be peculiar to the "drop measurement method." It is possible that electrical effects, and the effect of gases on the rapidity with which mercury vapour attains equilibrium with the liquid * may ultimately be shown to be important.

Summary.

The surface tension of mercury has been determined by the method of maximum bubble pressure. Investigations were made regarding the influence of the material of the tube used, the physical condition of the surface of the end of the tube from which the bubble is blown, and the nature of the gas used for blowing the bubbles. The effect of hanging the bubble on the end of the tube for various lengths of time and the time taken to blow the bubbles has also been examined.

Glass tubes appear to give slightly higher results than tubes made of silica, and in the case of the latter it was found that roughening the ends (tips) of the tubes was essential before concordant results could be obtained. This did not appear to be necessary with glass tubes. The nature of the gas used for blowing the bubbles, with the exception of oxygen, has practically no influence on the values found. Results could not be obtained with oxygen when glass tubes were used, but with silica tubes concordant values were found. With one set of glass tubes used, hanging the bubble on the end of the tube for various lengths of time always resulted in a lowering of the figure found, and this lowering increased with the length of the time. With another glass apparatus this effect was practically absent.

The phenomena described by Stöckle and Popesco is discussed, with special reference to the possible polymerization and surface orientation in liquid mercury.

The author would like to thank Dr. W. Rosenhain, F.R.S., for his continued interest in this work; Mr. G. D. Preston, B.A., and Mr. J. H. Awbery, B.A., B.Sc., for a number of suggestions; and Mr. J. Trotter for assistance in the experimental part of the work.

* Rideal, 'Surface Chemistry,' chap. 2, p. 60.

LI. *On the Ultra-Violet Radiations emitted by Point Discharges.* By JOHN THOMSON, M.A., B.Sc., Houldsworth Research Student in the University of Glasgow*.

Introductory.

IN recent papers † it has been shown that ionizing electromagnetic radiations similar to those discovered by Wiedemann are emitted by the gas in the vicinity of metallic points charged to a high potential. That such radiations (or radiations of slightly longer wave-length) may be of first importance in determining the mechanism of the spark discharge has been suggested by J. Taylor ‡, and the present writer § has described results which appear to support his theory. The experiments described in the present communication were undertaken with a view to obtaining further evidence regarding the nature of these radiations and their relation to the discharge. The experiments are of a preliminary nature, since, as far as the writer is aware, no attempt has so far been made to investigate any part of this region of the spectrum at pressures comparable with atmospheric. The results obtained, however, fully justify further study of the phenomena exhibited.

Experimental Arrangements.

The final form of the apparatus used in the investigation is represented diagrammatically in fig. 1.

The tube containing the points E and F between which the discharge was to pass was cylindrical in form, the platinum electrodes being placed along the axis of the cylinder. The detecting and measuring apparatus was contained in a side-tube placed opposite one of the platinum points E, while the other two side-tubes were fitted with stop-cocks K, H. One tube was branched between the stop-cock K and the discharge-tube.

The detecting apparatus consisted essentially of a photo-electric cell, the insulated electrode of which was connected to a tilted electroscope or to a Dolezalek electrometer. C and D were two half-cylinders of brass of length 20 mm.,

* Communicated by Prof. E. Taylor Jones, D.Sc.

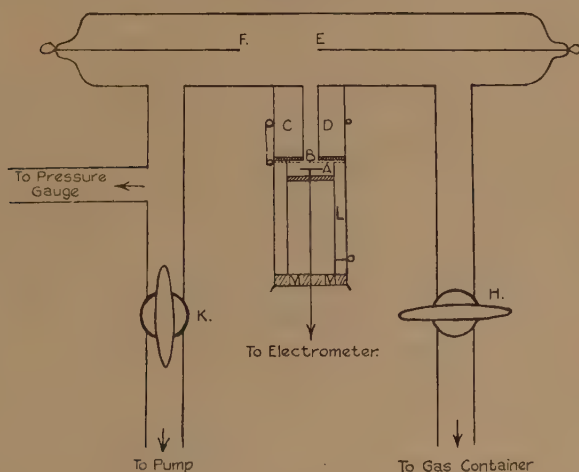
† C. E. Wynn-Williams, *Phil. Mag.* vol. i. p. 353 (1926); J. Thomson, *op. cit.* vol. v. p. 513 (1928).

‡ J. Taylor, 'Dissertation,' Utrecht (1927); *id.* *Proc. Roy. Soc. A*, vol. cxvii. p. 508 (1928).

§ J. Thomson, *loc. cit.*

sealed to the walls of the tube so that their faces formed the sides of a slot of width 4 mm. A potential difference of 560 volts was maintained between C and D during the course of the experiments. This strong electric field ($X=1400$ volts/cm.) was necessary in order to remove any ions which might drift or be projected down the slot towards the photo-electric cell. Theoretically the electric field was sufficiently strong to remove a simple positive molecular nitrogen ion projected into the slot with a speed of 3.10^7 cm./sec. Experiment showed that at pressures of 5 cm. of mercury and upwards no ions of any kind penetrated to the cell.

fig. 1.



B was a circular piece of fine-mesh phosphor-bronze wire gauze placed across the tube and insulated from C and D by two half-cylindrical plates of ebonite. This gauze formed one electrode of the cell. Pressed against it was the brass cylinder L which contained the other insulated electrode A. This electrode consisted of a small rectangular copper plate covered on the side facing the slot with a thin film of copper oxide. The latter, though less sensitive to ultra-violet light than other substances, suffers less from "photo-electric fatigue," and consequently could be relied upon to give results which would be comparable over a long period. This plate was placed at a distance of about 2 mm. from the gauze and soldered to a thin copper wire which was imbedded in pure paraffin wax and led down the axis of the

cylinder L to the electroscope or electrometer. The latter was placed at a distance of about 2 metres from the tube itself. It will be observed, therefore, that the insulated electrode and the lead (surrounded by earthed tubing) from it to the measuring instrument were well shielded from effects due to induction. This was tested experimentally before any measurements were made. The insulation also was tested, and proved to be of high quality. Finally, the side-tube containing this apparatus was completely sealed at M with a mixture of beeswax and resin.

The detecting cell therefore consisted of the gauze B, the cylinder L, and the insulated plate A, while the slot between C and D limited the radiation affecting it to a small pencil from the immediate vicinity of the point E. The connexions to C, D, and B were made by platinum wires sealed into the glass tube.

The other side-tubes provided a means of controlling the nature and pressure of the gas in the discharge-tube. One tube was connected through a capillary to a gas container, while the other was connected to an oil-pump. The branch in the latter tube was sealed to a vertical tube dipping into mercury, so that the pressure of the gas could be measured almost directly at any time. Since pressure measurements did not require to be very accurate, such a gauge was sufficient for the purpose. All the connexions were sealed with the beeswax mixture which was found to be very satisfactory for work at pressures greater than 0.1 mm. of mercury.

The potentials relative to the earth of the half-cylinders C and D, and of the gauze B and the cylinder L, depended on the particular nature and purpose of each experiment. When observations were being made with the tilted electroscope to measure the photo-electric or ionization current, the half-cylinder C, the gauze B, and the cylinder L were all at earth potential, while the plate A was charged to ± 12 volts. In the later experiments in which the Dolezalek electrometer was employed, C, B, and L were maintained at ± 250 volts, while the plate A was initially at earth potential.

The current across the discharge-tube was supplied by a large induction coil (10-inch spark) used in conjunction with a motor mercury jet interrupter. Such an arrangement, when used to produce peak potential differences corresponding to spark lengths of less than half an inch in air at atmospheric pressure, gives a remarkably steady mean current through the secondary of the coil. This current was measured by a Gaiffe milliamperemeter, and could be

controlled to 0.1 milliampere. In order to eliminate as far as possible any inverse current through the coil, the battery E.M.F. in the primary circuit was kept as small as possible. Experiment indicated that the current at "make" was negligible.

Four gases were employed in the experiments to be described—oxygen, carbon dioxide, nitrogen, and hydrogen,—and of these, only the two latter were used in quantitative investigations. The hydrogen and oxygen were prepared by electrolysis; the nitrogen was prepared by the action of ammonium chloride on potassium nitrite in concentrated solution, and was purified by passing it through concentrated sulphuric acid and over red-hot copper filings; the carbon dioxide was prepared by the action of dilute hydrochloric acid on marble chips. No attempt was made to dry any of these gases.

The instruments used to measure the ionization and photo-electric currents have already been mentioned. The tilted electroscope, being easy to adjust, was used in the preliminary investigations, but all the quantitative experiments were performed with the Dolezalek electrometer. The suspension used in the latter was a fine quartz fibre which was thoroughly platinized by placing it near the platinum-wire cathode in a low-pressure discharge. The conductivity of the suspension was thus permanently ensured, and it was verified that the sensitivity of the instrument remained constant. During the work to be described, the deflexion of the needle due to one volt potential difference between the quadrants corresponded to 960 mm. on the scale, which was 3 m. from the instrument.

Ionization and Photo-Electric Currents in Different Gases at Atmospheric Pressure.

(1) *Oxygen*.—No results were obtained in oxygen on account of a peculiar phenomenon exhibited by the gas. As this phenomenon is one which might invalidate any ionization experiments carried out in this gas, it may be well at this point to describe it briefly.

With the apparatus described in the previous section and the tilted electroscope as the detector of ionization, the normal conductivity of the gas at A was observed. This was very small. Then a spark discharge at atmospheric pressure was passed across the gas between E and F, a current of 1 milliampere flowing for about one minute. The discharge was then discontinued, and again the leakage of the electroscope was observed. It was found that the gas in the

vicinity of the insulated electrode A had become conducting, the rate of leakage of the electroscope being about one hundred times as great as before. The apparatus was now allowed to stand, the same gas was being left in the tube, and the rate of leak of the electroscope was read at half-hour intervals. The leakage gradually and consistently decreased, until, twenty-four hours after the passing of the discharge, the rate of leak was the same as that observed at the beginning of the experiment.

On account of the strong electric field in the slot between the half-cylinders C, D, it was impossible for any charged particles to penetrate from the discharge between E and F to the plate A. Hence it must be concluded that the conductivity of the gas at A was caused by ionization which took place in the vicinity of A. This conclusion was verified by another experiment performed in a specially constructed tube, where all the ions directly produced by the discharge were immediately removed by a strong electric field. Spontaneous ionization of the gas continued to take place for some hours after the discharge had passed.

It is suggested that this ionization accompanies the gradual change of the O_3 molecule (and perhaps others) formed during the spark discharge to the normal O_2 molecule. It is immediately obvious that no experiments on the ionization produced by electromagnetic radiation could be performed in this gas with the apparatus described.

(2) *Carbon Dioxide*.—The ionization and photo-electric currents in this gas were exceedingly small. At atmospheric pressure the current at A was comparable with the normal leakage of the apparatus, and consequently any observations taken would be of little value. Even at the comparatively low pressure of 30 cm. of mercury the currents were still small, and investigation of the effects in carbon dioxide was therefore postponed until a later date.

(3) *Nitrogen*.—This gas, when purified, showed no signs of the phenomenon just described as occurring in oxygen, but a trace of oxygen in the gas was sufficient to give an observable effect. The nitrogen was therefore purified and repurified until all trace of the effect had vanished. The first experiment was made for the purpose of obtaining a table of ionization and photo-electric effects from the vicinities of the anode and cathode in the discharge-tube. It was hoped that this table might be comparable with that given in a former paper *

* J. Thomson, *loc. cit.*

The tube was therefore filled with nitrogen at atmospheric pressure, all other gases having been excluded. The direction of the current in the primary of the coil was arranged so that E was the anode of the discharge, and readings were taken of the rate of leakage of the electroscope when the leaf, and therefore A, were charged to +12 and -12 volts relative to the earth. One milliampere was flowing from E to F. Then the direction of the current in the coil was changed, E becoming the cathode. The same readings were taken of the rate of discharge of A when charged to +12 and -12 volts. A great many difficulties were met with, one of the most important being the rise in temperature of the gas due to the discharge. Finally, the procedure adopted was to allow 15 minutes to pass between each reading of the ionization current, and to flood the discharge-tube with new gas before each reading. This allowed the tube to cool to room temperature between each discharge, and also eliminated any errors due to change in the chemical nature of the gas during the passage of the spark. The results, which have been verified with many samples of gas, are shown below; the figures in the last column are accurate to about 5 per cent.

Potential of A in volts.	Nature of E.	Rate of discharge of A.
+12	Anode.	4
+12	Cathode.	5
-12	Anode.	9
-12	Cathode.	9

Comparing these results with those obtained under different conditions and described in the above-mentioned paper, it must be concluded that the radiations in the two cases are of the same nature and have the same origin. Briefly, the differences between the two tables are exactly such as might have been anticipated from the differences in the conditions. In the experiment just described a current of one milliamperere was flowing in the discharge; in the former experiment the current was of the order of one microampere. The larger current might be expected (a) to intensify the radiations, (b) to partially level out the electric field in the gap, and so cause the intensity of the radiations from the vicinity of the cathode to increase. The first experiment was performed in air, the second in pure nitrogen. This appears to have caused little change in the total effect; and since these radiations are molecular or atomic properties, this is just what might be expected.

(4) *Hydrogen*.—Pure hydrogen, like nitrogen, is free from the spontaneous ionization effect observed in oxygen. The experiments performed in nitrogen, which have just been described, were repeated in hydrogen, and the table shown below indicates the results. The currents in hydrogen were larger than those in nitrogen, and the figures in the last column can be compared directly with the corresponding figures for nitrogen.

Potential of A in volts.	Nature of E.	Rate of discharge of A.
+12	Anode.	4
+12	Cathode.	8
-12	Anode.	6
-12	Cathode.	16

Variation of Ionization and Photo-Electric Currents with Pressure in Different Gases.

The next series of experiments was designed to show how the effects of the radiations from each gas varied with the pressure of the gas. The experimental arrangements which have already been described were used, the Dolezalek electrometer being adopted as the current-measuring instrument. Readings were taken of the ionization and photo-electric currents at A, the insulated electrode, at different pressures, when one milliamperé was flowing across the gas between E and F. Two sets of readings were taken: (i.) when the gauze B and cylinder L were at -250 volts relative to A; (ii.) when the gauze B and cylinder L were at $+250$ volts relative to A. In all cases E was made the cathode, as it was found that the currents from the anode were unsteady.

In case (i.) the currents measured by the electrometer represented the ionization currents at A. No photo-electric effect took place owing to the large negative potential of B; any photo-electrons emitted by B travelled to D under the action of the stronger electric field between B and D. Also since the field between A and B was 1250 volts/cm., the current measured was the saturation current for the gas, and was directly proportional to the number of ions formed between A and B.

In case (ii.) the currents measured by the electrometer represented the sum of the photo-electric and ionization effects, each giving its saturation current. Therefore, by subtracting the readings taken under conditions (i.) from the corresponding readings taken under conditions (ii.), it

was possible to obtain a measure of the pure photo-electric effects of the radiations.

The procedure while taking these observations was important, as on it depended the reliability of the results. It was as follows :—

(a) With the insulated quadrant of the electrometer earthed, and all the electrical connexions to C, D, B, and L broken, the discharge-tube was exhausted.

(b) The tube was flooded with the pure gas to the required pressure.

(c) The connexions to C, D, B, L were made and the discharge across EF was started, the current being adjusted to one milliampere.

(d) The pressure of the gas was observed.

(e) The electrometer quadrant was insulated, and the ionization current was read by noting the time taken by the image to move over 150 divisions on the scale.

(f) The quadrant was earthed and the pressure of the gas observed. The pressure at the time of reading the ionization current was the mean of the two observations.

(g) The discharge was stopped and the apparatus allowed to stand for 15 minutes.

This procedure was repeated with every observation of the current and pressure.

Hydrogen.—In fig. 2 below are given the curves obtained in hydrogen by the experiments just described. The ordinate represents in the case of curve (a) the ionization current, in the case of curve (b) the ionization current plus the photo-electric current. Curve (c) has been obtained by subtracting the ordinate of (a) from the ordinate of (b), and therefore represents the photo-electric current alone.

Nitrogen.—The corresponding curves for nitrogen are shown in fig. 3. Again (a), (b), (c) refer to ionization current, ionization current plus photo-electric current, and pure photo-electric current respectively. The scales in figs. 2 and 3 are the same, so that the relative effects in the two gases are shown directly.

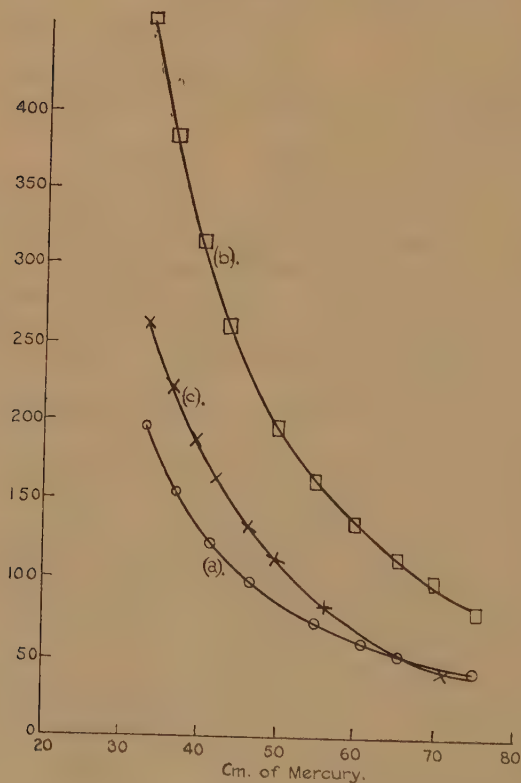
Variation of Ionization Current with Discharge Current.

The next experiments were performed to investigate how the ionization current at A varied with the current flowing between E and F, the pressure being kept constant. These observations were made in the same manner as those already described, viz. a new sample of gas was used at each reading, and the gas was kept at room temperature by allowing

a 15 minutes' pause after each observation. The results are indicated by the curves shown below (fig. 4), where the abscissa measures the current across EF in milliamperes, and the ordinate the ionization current in arbitrary units.

Curves (a) and (b) refer to nitrogen, (a) being taken at a pressure of 25 cm. of mercury and (b) at a pressure of

Fig. 2.



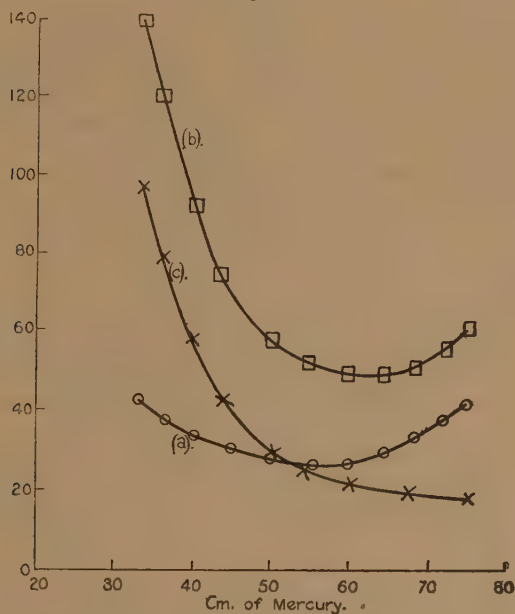
33 cm. Curves (c) and (d) refer to hydrogen. (c) was taken at 37 cm. and (d) at 48 cm. All these curves were obtained with the gauze system charged to -250 volts so that no photo-electric effect could take place.

Variation of Peak Potential across EF with Pressure.

The arrangement used for determining the peak potential across the discharge-tube was a spark-gap placed in parallel with the discharge. The electrodes of the gap were

zinc spheres of diameter 2.5 cm., carefully cleaned with fine emery-paper. The discharge across EF was maintained at one milliampere and the pressure of the gas was observed. Then the spark-gap was slowly closed until a spark just passed. The pressure of the gas was again observed and the discharge stopped. The parallel gap was measured to .005 cm. by means of a reading microscope. The pressure of the gas was the mean of the two readings taken. The results for this series of observations in nitrogen and

Fig. 3.



hydrogen are shown below (fig. 5), where the ordinate represents the peak potential across the gap in kilovolts, and the abscissa the pressure in cm. of mercury.

Discussion of Experimental Results.

The Ionizing Potentials of Hydrogen.—The ultra-violet spark spectra of hydrogen are well known. Under different conditions the gas emits two line spectra, stretching from 1670 to 900 A.U., and two continuous spectra. There is still considerable doubt as to the lowest ionizing potential of the gas. Many observers record ionization occurring at a

Fig. 4.

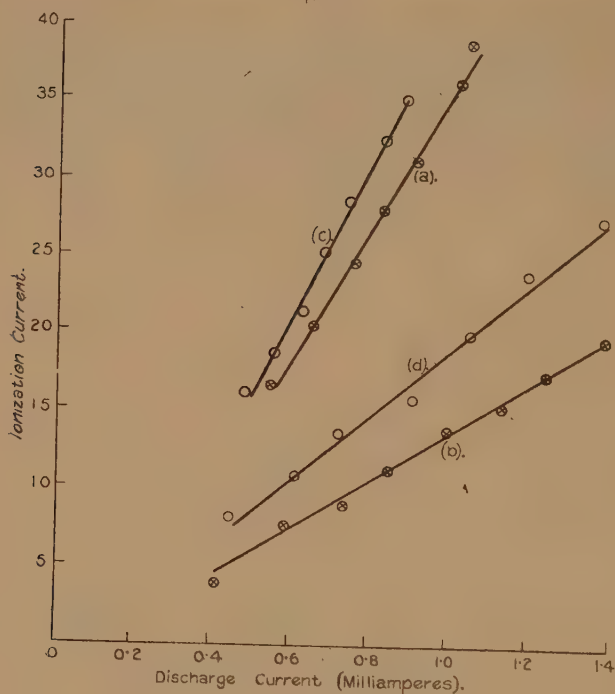
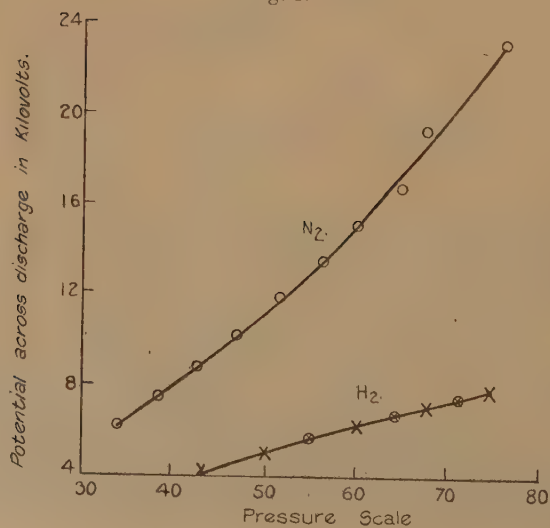


Fig. 5.



potential of 11 volts, but this value has been questioned by Horton and Davies*, who suggest that it is due to the presence of mercury vapour in the apparatus. The most generally accepted lowest value is 16 volts, which is said to correspond to the formation of H_1^+ and H_1^- from H_2 ; that is, to ionization plus dissociation. F. L. Mohler†, on the basis of his own experiments, concludes that "there is no evidence that hydrogen emits radiation which is capable of ionizing the normal molecule," and, as he points out, since no hydrogen lines have been observed beyond 885 A.U., this appears reasonable if the lowest ionizing potential is 16 volts. All the experiments performed in hydrogen and described in the present paper, however, indicate a strong ionization of the gas by its own radiations. Nor was this effect due to water-vapour content in the gas, for the same experiments were performed with identical results in gas which had been carefully dried. The water-vapour was only allowed to remain in the gas during the remainder of the experiments because it was found that it caused no perceptible alteration in any of the observations. Whether the observed ionization was due to the H_3 ion, or even to the H_1 ion, cannot be definitely stated. It seems improbable, however, that at pressures comparable with atmospheric such molecules should exist in sufficient numbers to account for the comparatively large currents which were measured. The conclusion suggested is that either hydrogen possesses a lower ionizing potential than the accepted one (16 volts), or the gas is capable of emitting radiations of shorter wavelength than those examined until the present. If the latter conclusion is correct, the radiations are molecular in origin, since the limit of the Lyman series, $N\left(\frac{1}{1^2} - \frac{1}{m^2}\right)$, which is the atomic radiation of greatest frequency, corresponds to a potential of 13.5 volts.

Variation of the Ionization Current with the Discharge Current, the Pressure being Constant.—The ordinates of the curves collected in fig. 4 measure the ionization currents at A. Since the pressure remained constant, and the currents measured were of saturation value, they may be taken to represent the intensities of the ionizing radiations. Therefore the curves show the variation of the intensity of the radiations with the current flowing between E and F. They indicate quite definitely that the intensity of these

* Phil. Mag. vol. xlvi. p. 872 (1923).

† Proc. Nat. Acad. Sci. xii. p. 494 (1926).

radiations increases linearly with the discharge current. Therefore, if it is assumed that the mean frequency of the radiations does not change with change in the current density, it may immediately be stated that, since the potential across EF remains constant, *the pressure of the gas being constant, a constant fraction of the energy dissipated in the discharge (for the energies investigated) is transformed into ionizing electromagnetic radiation.*

Whether this remains true for very large or very small currents still remains to be investigated, but certain significant points emerge from a consideration of the curves already obtained. The gradients of the lines (a) and (c) are definitely greater than the gradients of the lines (b) and (d), while the curves, if produced, cut the discharge current axis at different points. The difference between the two sets of curves is that (a) and (c) were taken at a lower pressure than (b) and (d).

The fact that the gradients of the curves (a) and (c) are greater than the gradients of the curves (b) and (d) is suggestive. This means that, as the pressure diminishes, the same increase in the current density at E produces a larger increase in the radiations detected at A. This may be due to either or both of the following causes:—

(i.) Owing to the increase in the mean free paths of the gas ions with the decrease in the pressure, a greater percentage of the total number of ions carrying the current may excite radiation in the gas. If this is correct, the total intensity of the radiations at their source will increase as the pressure is diminished, a constant current being maintained across EF.

(ii.) The same change in the intensities of the radiations may occur at the source at all pressures, when the discharge current is changed by the same amount, but the change in the intensity at A will be smaller the higher the pressure, owing to the greater absorbing power of the gas.

No matter what the cause of these variations is, it is at least evident, as has been shown, that, for the currents investigated, $C = Li + M$, where C is the ionization current measured at A, and i is the current flowing across EF. L and M are constants when the pressure is constant, but L at least must be a function of the pressure, p . Taking the simplest assumption first, let

$$C = i\phi(p).$$

Then

$$\frac{\partial C}{\partial i} = \phi(p),$$

and therefore

$$\frac{\frac{\partial C}{\partial i}]_{p=p_1}}{\frac{\partial C}{\partial i}]_{p=p_2}} = \frac{\phi(p_1)}{\phi(p_2)} = \frac{C_1}{C_2}]_{i=\text{constant}} = \frac{m_1}{m_2},$$

where m_1 is the gradient of the line $C=i\phi(p_1)$, and m_2 is the gradient of the line $C=i\phi(p_2)$. But from the curves of figs. 2 and 3, $\frac{C_1}{C_2}$ may be determined. For the case of hydrogen $\frac{m_1}{m_2} = 2.9$, while $\frac{C_1}{C_2} = 1.7$ for corresponding pressures. Therefore C is not of the form $C=i\phi(p)$. The supposition that $C = (i-K)\phi(p)$ is no more tenable, for again

$$\frac{C_1}{C_2}]_{i=\text{constant}} = \frac{m_1}{m_2}.$$

It is therefore evident that the true form of the function must be

$$C = i\phi(p) - \psi(p). \quad . \quad . \quad . \quad . \quad (1)$$

Then

$$\frac{\partial C}{\partial i} = \phi(p)$$

and

$$\frac{m_1}{m_2} = \frac{C_1 + \psi(p_1)}{C_2 + \psi(p_2)}.$$

If

$$\psi(p_1) > \psi(p_2),$$

in general

$$\frac{m_1}{m_2} > \frac{C_1}{C_2}.$$

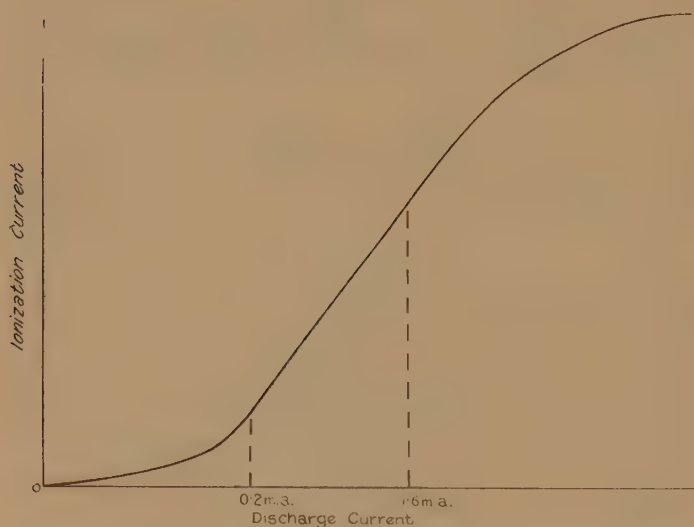
The graphs of fig. 4 indicate that $\psi(p_1) > \psi(p_2)$, and are therefore in agreement with this hypothesis. It may at this point be remarked that it is proposed in later work to evaluate $\psi(p)$ for many different values of p by observations similar to those shown in fig. 4. In this way it is hoped that the forms of both functions will be exhibited. Reasons will be given later which suggest that the form of $\frac{\phi(p)}{\psi(p)}$ should be interesting.

It must be observed that the theory which has just been given only applies to a limited range of discharge current (0.4 to 1.5 milliamperes). It is very improbable that the linear relation between C and i will hold for small currents,

as C would then be zero when $i = \frac{\psi(p)}{\phi(p)}$. Possibly the complete form of the C, i curve is as shown below in fig. 6.

Variation of Ionization and Photo-electric Currents with Pressure in Different Gases.—Figs. 2 and 3 represent the variation with pressure of the currents at A in hydrogen and nitrogen respectively. The pressures were varied from about 76 cm. of mercury to about 30 cm., as this region was the most difficult to investigate (owing to the small values of the currents) and at the same time the most interesting.

Fig. 6.



The curves in nitrogen are entirely different from those in hydrogen, except perhaps in the case of the curves giving the pure photo-electric effects, which are at least similar in form. The currents in hydrogen continually decrease with increase of pressure; both experimental curves in nitrogen exhibit a decided minimum at about 60 cm. of mercury.

As the problem of interpreting and, if possible, explaining these results is exceedingly complicated, it may be well to state at the outset in the most general terms the variables in the experiments. Broadly speaking, the variation with pressure of any radiations detected at A might be due to three factors, which are as follows:—

- (i.) Change in the total absorption of the gas between E and A.
- (ii.) Changes in the intensities of the radiations at their source E.
- (iii.) Changes in the frequencies of the radiations emitted at E.

Of these factors (i.) is likely to be of the greatest and (iii.) of the least importance, while (ii.) and (iii.) may be grouped together as changes in the character of the radiations from E.

Concerning the absorption of the gas between E and A, it is necessary to consider first how a monochromatic ultra-violet radiation of constant intensity I_λ at its source would vary in intensity at A as the pressure of the intervening gas is changed. It is well known that, for the visible spectrum and also for the X-ray region, the intensity at A might be represented by the expression $I_\lambda e^{-\alpha p}$, where p denotes the pressure of the gas, and α is a function of the frequency of the radiation. But for the region with which these experiments are concerned, namely that region producing intense ionization of the gas, this expression has not been verified; while for certain analogous cases concerned with the absorption of ultra-violet light by solutions, it is known that α is also a function of the concentration of the absorbing medium.

Let it be assumed, however, that the absorption of the radiation occurs according to the normal law. Let the loss of energy across a distance dx of the total distance EA be proportional to

- (i.) the intensity of the radiation at that point, I ;
- (ii.) the density of the gas at that point, ρ .

Also let the constant of proportionality (the absorption-coefficient) be a function of the wave-length of the light, $\phi(\lambda)$.

Then
$$dI = -\phi(\lambda)\rho I dx,$$

$$I = I_\lambda e^{-\phi(\lambda)kpx},$$

where $\rho = kp$.

But the ionization current C is proportional to the loss of energy, as the radiation passes through 2₁ mm. of the gas near A.

$$dI = -\phi(\lambda)kpI_\lambda e^{-\phi(\lambda)kpx} dx.$$

$$\therefore C = Kp\phi(\lambda)e^{-kpd\phi(\lambda)}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where d is the distance EA.

Therefore, if the radiation from the vicinity of E were monochromatic, the current C would be a function of p of the form $C = \alpha p e^{-\alpha p}$, having a maximum where $p = \frac{1}{\alpha}$.

Needless to say, the radiations from A are not monochromatic, and the simple theory given above might be expected to be inapplicable to the experimental results on this ground alone. If, for example, the gas is supposed to emit a continuous spectrum, the absorption-coefficient in the above analysis will not take a mean value for the spectrum. As the pressure is diminished, the relative intensities at A of the different parts of the spectrum will vary, owing to the dependence of α upon λ . If the law of variation of spectrum intensity at the source is $I_\lambda = F(\lambda)$, then the intensity of the spectrum at A will be given by

$$I = F(\lambda) e^{-\phi(\lambda) k p d},$$

and if the spectrum is continuous between the limits $\lambda = \lambda_1$ and $\lambda = \lambda_2$ (analogous to an X-ray impulse spectrum* where the intensity at λ_2 is very small), the total effect at A in terms of ionization current is

$$C = K \int_{\lambda_1}^{\lambda_2} p F(\lambda) \phi(\lambda) e^{-k p d \phi(\lambda)} d\lambda. \quad (3)$$

Any attempts to evaluate $\phi(\lambda)$ and $F(\lambda)$ at this stage of the investigation must necessarily be purely hypothetical; but if it is assumed that the gas is a simple resonator of resonating wave-length λ_0 , then, where no damping coefficient is introduced,

$$\phi(\lambda) = \frac{N \lambda^4}{(\lambda^2 - \lambda_0^2)^2}.$$

Similarly, if it is assumed that the continuous spectrum is *exactly* analogous to the X-ray spectrum, beginning at $\lambda = \lambda_0$ and dying away towards $\lambda = 2\lambda_0$,

$$F(\lambda) = \frac{(2\lambda_0 - \lambda)(\lambda - \lambda_0)}{\lambda_0^2}.$$

and

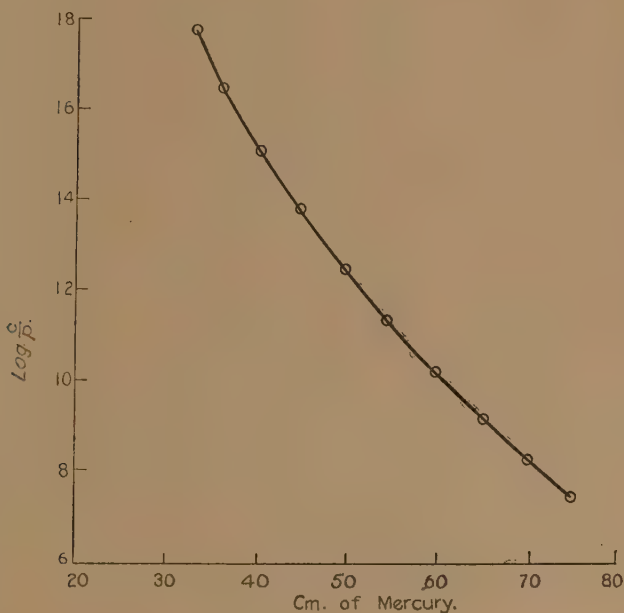
$$C = K \int_{\lambda_0}^{2\lambda_0} p \frac{(2\lambda_0 - \lambda)(\lambda - \lambda_0) \lambda^4}{\lambda_0^2 (\lambda^2 - \lambda_0^2)^2} e^{-\frac{k p d \lambda^4}{(\lambda^2 - \lambda_0^2)^2}} d\lambda. \quad (4)$$

* C. T. Ulrey, *Phys. Rev.* ii. p. 401 (1918).

Neither equation (3) nor (4) can be used until more is known concerning the variables involved, and until they can be combined with the variations in intensity due to changes in the emissive power of the gas, for both are concerned wholly with absorption effects.

Qualitatively, however, the reduction of pressure might be expected by the above theory to increase the current C . Certainly no minimum is to be expected in the curve, although a maximum is predicted by equation (2) at a pressure probably much below those investigated in the

Fig. 7.



present experiments. The hydrogen curve (α) is not inconsistent with such a theory. The increase in the current with diminution of pressure is approximately according to the formula

$$C = Ape^{-\alpha p}, \quad (2)$$

a small but consistent increase in the coefficient α being evident. Fig. 7, below, exhibits the variation of $\log \frac{C}{p}$ with pressure for the curve (α) (fig. 2).

So far the variables (ii.) and (iii.) in the experiments have been neglected. The shape of curve (a) (fig. 2) has been examined wholly from the point of view of the absorption of the gas, and it has been implicitly assumed that the effects of variations in the intensities of the radiations at their source were negligible compared with the absorption effects. It now remains to be seen whether this assumption is justifiable or not.

Theoretically the reduction in pressure might be expected by increasing the mean free paths of the ions to increase the probability of excitation of the shorter wave radiations. On the other hand, the decrease in the potential necessary to carry the discharge which accompanied the decrease of pressure might cause a corresponding fall in the potential drops across the free paths of the ions. As the mean free path λ is inversely proportional to the pressure, and the potential, as shown from fig. 5, is approximately proportional to the pressure, the product $X\lambda$ might be expected to remain constant, on the assumption that the field X in the vicinity of E is proportional to the potential across EF . If, however, the field at E is that due to the normal cathode fall, and is independent of the pressure, the probability of radiation accompanying the impact of ions must be inversely proportional to the pressure. Again, if the radiations are due to the impact of ions on neutral molecules, another point must be considered. For a given ionic current the number of molecules in the gap EF and therefore the probability of radiation will be proportional to the pressure. If the radiations are due both to ionic and molecular collisions, the expression for the intensity at the source will be the sum of *two* functions of the pressure.

In the preceding investigation it was found that the current at A was given by equation (1) :

$$C = i\phi(p) - \psi(p), \dots \dots \dots (1)$$

where $\frac{d\psi}{dp}$ was negative. This indicates that an important

fraction of the radiation is due to the impact of ions on neutral molecules, since no other hypothesis could explain the existence of $\psi(p)$. If the simplest possible interpretation be given to the variation with pressure of the intensity I_λ of the radiations at their source

$$I_\lambda = Ai - \frac{B}{p}.$$

Then assuming the theory leading to equation (2),

$$C = (Aip - B)e^{-ap}$$

and

$$\phi(p) = Ape^{-ap}, \quad \psi(p) = Be^{-ap}.$$

No matter what functions of p are used in the expression for I_λ , since $C = pl_\lambda e^{-ap}$, it is quite reasonable to assume that the absorption term e^{-ap} will be the most important; this explains why the absorption effects could be considered alone in the case of hydrogen.

To return to the absorption of the radiations, in the case of curve (a) for nitrogen, the theory which has been sketched does not apply. The absorption of nitrogen cannot follow the simple laws which appeared to fit the case of hydrogen, or else the quality of the radiations from the discharge must vary with the pressure in a peculiar manner. It has certainly been observed that the visible radiations from the discharge in hydrogen are entirely different from those in nitrogen. The greater part of the spark in hydrogen is blue in colour, *and its colour does not alter as the pressure is diminished*. The spark in nitrogen at atmospheric pressure emits radiations of all colours, and consequently appears white, *but as the pressure is reduced the discharge becomes almost entirely red*. This may mean a shift of the maximum intensity of the radiations towards the red end of the spectrum; it may mean that the absorption of the gas has changed in such a way as to cut off the blue light. Neither explanation appears probable, but either is consistent with the curves (a) and (b) of fig. 3.

That the maximum intensity of the radiations should shift towards the red end of the spectrum as the pressure is diminished is contrary to the results obtained by L. Hamburger*, who found that for the visible spectrum the maximum of the emitted light from nitrogen shifted towards the ultra-violet as the pressure was diminished. His experiments were, however, performed at a very much lower pressure than those described in the present communication. It must also be observed that the curve (c) (fig. 3), which gives the variation with pressure of the intensities of the radiations producing the photo-electric effects at A, exhibits no minimum. Although the curve is not by any means exponential, there is a steady increase in the intensity as the pressure is reduced. This difference between the ionization-current

* K. Akad. Amsterdam, xx. Proc. 7, p. 1043 (1918).

curve and the photo-electric current curve must be significant. It indicates that if the anomalous variation in curve (c) is due to absorption, the anomalous absorption affects only the shorter wave radiations, and then it is difficult to see why the appearance of the discharge should alter as the pressure is reduced. On the other hand, it agrees well with the hypothesis that the maximum intensity of the radiations moves towards the infra-red, for then the photo-electric effect, being due to radiations of longer average wave-length than those causing the ionization effects, would suffer little change. On the whole, the evidence indicates that the difference between the curves for nitrogen and hydrogen is not due to the gases obeying different absorption laws, but is due rather to the difference between the modes of variation with pressure of the radiations emitted by the gases.

Summary.

Preliminary experiments are described showing:—

1. The variation with pressure of the ionizing and photo-electric radiations from hydrogen and nitrogen when the gases are excited by a discharge.
2. The variation of the intensity of these radiations when the pressure is kept constant and the discharge current is varied.

The curves obtained depend upon both absorption and emission variations, and an attempt is made to estimate the relative importance of the two effects, and so to separate them. Tentative explanations are offered of the various phenomena, and it will be a matter for further investigation to decide between them.

Reasons are put forward suggesting that the radiations are molecular in origin.

A spontaneous ionization phenomenon in oxygen is described and an explanation is offered.

In conclusion, the writer again wishes to express his thanks to Professor Taylor Jones for his encouragement and advice, which have proved invaluable. The work was performed in the Research Laboratories of the Natural Philosophy Department of the University of Glasgow.

July 1928.

LII. *Mathieu Functions of Stable Type.*

By E. L. INCE, M.A., D.Sc.*

1. *Introduction.*

THE general solution of the Mathieu equation †.

$$\frac{d^2y}{dx^2} + (\eta - 2\theta \cos 2x)y = 0, \quad . \quad . \quad . \quad (1)$$

is known from theoretical considerations to be of the form

$$y = Ae^{\mu x}\phi(x) + Be^{-\mu x}\phi(-x), \quad . \quad . \quad . \quad (2)$$

where $\phi(x)$ has the period π . The two main problems which arise are (a) the determination of η , for a given θ , such that the equation shall have a solution of assigned periodicity, and (b) the determination of μ when η and θ are given. The first problem has been solved by the present writer ‡, and tables of the functions of periods π and 2π will in due course be available. The second problem will now be considered.

When μ is a pure imaginary, the solution is said to be *stable*; otherwise it is *unstable*. When θ is zero, a stable solution exists for every positive value of η , but as θ increases, the probability that a solution with η chosen at random shall be stable diminishes rapidly. This is shown very clearly in fig. 1. The curves $a_0, b_1, a_1, b_2, \dots$ represent the determinations of η corresponding to the elliptic cylinder functions $ce_0(x), se_1(x), ce_1(x), se_2(x), \dots$. The regions between a_0 and b_1 , between a_1 and b_2 , and so on, for θ positive, and the symmetrical regions for θ negative, are the regions of stability, and since the bounding curves tend rapidly to coincidence, the above statement is justified. The diagram furnishes a rough guide as to whether the solution corresponding to any value-pair (θ, η) is stable or not. Naturally, in physical problems the stable solutions are the more interesting.

Several methods of determining the index μ have been

* Communicated by the Author.

† This form of the Mathieu equation differs slightly from the form generally in vogue, but it has been adopted as the standard in the computation of the elliptic cylinder functions which is now in progress. In the majority of physical applications θ is positive.

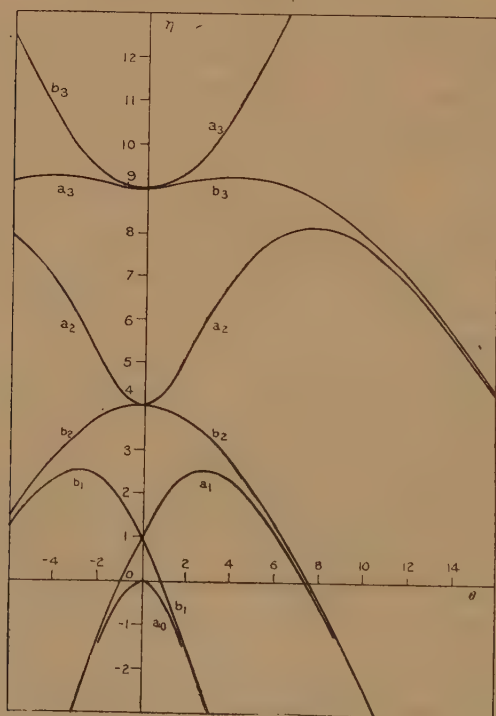
‡ Proc. Roy. Soc. Edin. xlv. pp. 20-29, 316-322 (1925-26); xlvii. pp. 294-301 (1927).

devised ; the latest is that due to Whittaker *. The essential point of his method is to express η and μ in the forms

$$\eta = F(\sigma), \quad \mu = G(\sigma),$$

where $F(\sigma)$ and $G(\sigma)$ are respectively even and odd Fourier series in σ whose coefficients depend only on θ . The first equation is solved numerically for σ ; the second then gives

Fig. 1.



μ immediately. This method is of practical value, and has, in fact, been applied to G. W. Hill's classical problem in the lunar theory. The numerical work is, however, laborious, and is complicated by the fact that in the stable case σ is either purely imaginary or a complex number of the form $\frac{1}{2}\pi + \tau i$. For that reason the following method is to be preferred in practice whenever the solution is known to be stable

* Proc. Edin. Math. Soc. xxxii. pp. 75-80 (1914).

2. The General Solution.

The Mathieu equation is satisfied by a solution of the form

$$y = \sum_{-\infty}^{\infty} e_r \cos (2r + \rho)x, \quad . \quad . \quad . \quad . \quad (3)$$

provided that the coefficients e_r satisfy the recurrence-relations

$$\{\eta - (2r + \rho)^2\}e_r = \theta(e_{r-1} + e_{r+1}) \quad . \quad . \quad . \quad (4)$$

for all integral values of r , and provided that these relations are consistent. There is evidently no loss of generality in assuming that $0 \leq R(\rho) < 1$, where $R(\rho)$ denotes the real part of ρ . When the solution is stable, ρ is real.

Equation (1) is unchanged if x is replaced by $\pi - x$. Consequently, when the solution (3) exists, there also exists the solution

$$\begin{aligned} y &= \sum_{-\infty}^{\infty} e_r \cos (2r + \rho)(\pi - x) \\ &= \cos \rho \pi \sum_{-\infty}^{\infty} e_r \cos (2r + \rho)x + \sin \rho \pi \sum_{-\infty}^{\infty} e_r \sin (2r + \rho)x, \end{aligned}$$

which is distinct from (3) except when ρ is an integer or zero.

With these exceptions, therefore, there is always associated with (3) the solution

$$y = \sum_{-\infty}^{\infty} e_r \sin (2r + \rho)x. \quad . \quad . \quad . \quad . \quad (5)$$

Conversely (3) is associated with (5) except when ρ is an integer or zero. These solutions are evidently distinct and form a fundamental pair. Thus, setting aside the special cases which arise when ρ is an integer or zero, equation (1) has a general solution of the form

$$y = A \sum_{-\infty}^{\infty} e_r \cos (2r + \rho)x + B \sum_{-\infty}^{\infty} e_r \sin (2r + \rho)x,$$

which is not essentially different from (2). The number ρ is determined by the condition that the recurrence-relations be consistent.

If $\rho = 1$, the recurrence formula for $r = n$ is the same as that for $r = -n - 1$, and it is an easy matter * to prove that

* Express e_{-1}/e_0 as a continued fraction in two distinct ways as in the following section; this shows that $e_{-1} = \pm e_0$, and the rest follows immediately.

$e_{-r-1} = \pm e_r$. If $e_{-r-1} = e_r$, then (5) becomes identically zero, and (3) may be written

$$y = \sum_0^{\infty} c_r \cos(2r+1)x,$$

where $c_r = 2e_r$. For $r \geq 1$, c_r follows the same recurrence-relation as e_r , but for $r=0$ the relation becomes

$$(\eta - \theta - 1)c_0 = \theta c_1.$$

The solution is thus a multiple of an elliptic cylinder function of the type $ce_{2m+1}(x, \theta)$. If $e_{-r-1} = -e_r$, (3) becomes identically zero, and (5) may be written

$$y = \sum_0^{\infty} c_r' \sin(2r+1)x,$$

where $c_r' = 2e_r$. The recurrence-relation for c_r' is the same as that for c_r when $r \geq 1$, but when $r=0$ it becomes

$$(\eta + \theta - 1)c_r' = \theta c_1'.$$

Thus the solution is a multiple of an elliptic cylinder function of the type $se_{2m+1}(x, \theta)$. The case $\rho=1$ virtually includes the case where ρ is any odd integer.

If $\rho=0$, the recurrence-relation for $r=n$ is the same as that for $r=-n$, and it is easily proved that $e_{-r} = \pm e_r$. If $e_{-r} = e_r = \frac{1}{2}c_r$, (5) becomes identically zero and (3) may be written

$$y = \frac{1}{2}c_0 + \sum_1^{\infty} c_r \cos 2rx.$$

For $r > 1$, c_r follows the same recurrence-relation as e_r , but for $r=0$ the relation becomes

$$\eta c_0 = 2\theta c_1.$$

The solution is thus a multiple of an elliptic cylinder function of type $ce_{2m}(x, \theta)$. Similarly, if $e_r = -e_{-r} = \frac{1}{2}c_r'$, (3) disappears and (5) may be written

$$y = \sum_1^{\infty} c_r' \sin 2rx.$$

For $r > 1$ the recurrence-relation is as before, but with $c_0' = 0$. The solution is thus a multiple of an elliptic cylinder function of type $se_{2m}(x, \theta)$. The case $\rho=0$ virtually includes the case where ρ is an even integer.

It is clear that in the general case $\sum e_r \neq 0$, for if the contrary were true, then both (3) and its first derivative would vanish for $x=0$, which is impossible since the origin is an ordinary point of equation (1). Thus, if necessary, the solutions (3) and (5) may be made definite by the assumption $\sum e_r = 1$.

3. The Conditions for Consistence.

The recurrence-relation (4) may be written in the form

$$\begin{aligned} \frac{e_r}{e_{r-1}} &= \frac{\theta}{\eta - (2r + \rho)^2 - \theta \frac{e_{r+1}}{e_r}} \\ &= \frac{-\theta(2r + \rho)^{-2}}{1 - \eta(2r + \rho)^{-2} + \theta(2r + \rho)^{-2} \frac{e_{r+1}}{e_r}}, \end{aligned}$$

and may consequently be expressed as an infinite continued fraction depending upon r , ρ , θ , and η . It will be useful to have a compact notation for an infinite continued fraction whose successive partial quotients are determined by a definite law; let

$$\Phi_n^{\infty} \frac{\alpha_r}{\beta_r}$$

represent the continued fraction *

$$\frac{1}{\beta_n} + \frac{\alpha_{n+1}}{\beta_{n+1}} + \frac{\alpha_{n+2}}{\beta_{n+2}} + \dots$$

Consequently

$$\left. \begin{aligned} \frac{e_n}{e_{n-1}} &= -\theta(2n + \rho)^{-2} \Phi_n^{\infty} \frac{-\theta^2(2r + \rho)^{-2}(2r + \rho - 2)^{-2}}{1 - \eta(2r + \rho)^{-2}} \\ &= -\theta(2n + \rho)^{-2} \Phi_0^{\infty} \frac{-\theta^2(2r + 2n + \rho)^{-2}(2r + 2n + \rho - 2)^{-2}}{1 - \eta(2r + 2n + \rho)^{-2}}. \end{aligned} \right\} \quad (6)$$

But the recurrence-relation may also be written as

$$\begin{aligned} \frac{e_{r-1}}{e_r} &= \frac{\theta}{\eta - (2r + \rho - 2)^2 - \theta \frac{e_{r-2}}{e_{r-1}}} \\ &= \frac{\theta(2r + \rho - 2)^{-2}}{1 - \eta(2r + \rho - 2)^{-2} + \theta(2r + \rho - 2)^{-2} \frac{e_{r-2}}{e_{r-1}}}, \end{aligned}$$

and consequently

$$\frac{e_{n-1}}{e_n} = -\theta(2n + \rho - 2)^{-2} \Phi_1^{\infty} \frac{-\theta^2(2n - 2r + \rho)^{-2}(2n - 2r + \rho + 2)^{-2}}{1 - \eta(2n - 2r + \rho)^{-2}}. \quad (7)$$

Note that the leading numerator is *unity*. Note also that

$$\Phi_n^{\infty} \frac{\alpha_r}{\beta_r} = k_n \Phi_n^{\infty} \frac{k_r \alpha_r}{k_r \beta_r},$$

if both members converge.

The last equation may be transformed by the relation

$$\frac{e_n}{e_{n-1}} = \frac{\eta - (2n + \rho - 2)^2}{\theta} - \frac{e_{n-2}}{e_{n-1}}$$

into

$$\frac{e_n}{e_{n-1}} = \frac{\eta - (2n + \rho - 2)^2}{\theta} + \theta(2n + \rho - 4)^{-2} \Phi_2^{\infty} \frac{-\theta^2(2n - 2r + \rho)^{-2}(2n - 2r + \rho + 2)^{-2}}{1 - \eta(2n - 2r + \rho)^{-2}}. \quad (8)$$

When θ , η , n , and ρ are finite,

$$\alpha_r \rightarrow 0, \quad \beta_r \rightarrow 1$$

in each continued fraction, therefore each continued fraction converges; moreover, as n increases, each tends to the limit unity*.

The condition for the consistence of the recurrence-relations is that (6) and (8) should give equal values to e_n/e_{n-1} . In particular, when $n=1$, let

$$L = -\frac{e_1}{e_0} = \frac{\theta}{(\rho+2)^2} \Phi_0^{\infty} \frac{-\theta^2(2r+\rho+2)^{-2}(2r+\rho)^{-2}}{1-\eta(2r+\rho+2)^{-2}},$$

$$R = -\frac{e_1}{e_0} = \frac{\rho^2-\eta}{\theta} - \frac{\theta}{(\rho-2)^2} \Phi_2^{\infty} \frac{-\theta^2(2r-\rho-2)^{-2}(2r-\rho-4)^{-2}}{1-\eta(2r-\rho-2)^{-2}}.$$

Then the condition of consistence is $L=R$.

In order to apply this condition in any particular case when θ and η are given, tentative values of ρ are inserted in the continued fractions, and L and R are calculated. The result indicates how ρ is to be adjusted to secure numerical equality between L and R . When this end has been attained, not only has the value of ρ been obtained to the desired degree of precision, but material has been accumulated from which the ratios of consecutive coefficients in the expansion of the solution may easily be deduced. How the method is carried out in practice will be shown in the following section.

4. Numerical Example.

When the use of the Mathieu functions becomes more general than it is in the present day, it will be necessary to have at hand tables showing the value of ρ for outstanding values of θ and η . These tables would indicate a suitable initial value of ρ , for any assigned value-pair (θ, η) , on

* Perron, 'Die Lehre von den Kettenbrüchen,' § 56.

which the accurate calculation of ρ would be based. As things are at present, every value of ρ must be calculated *ab initio*.

As an example of the method, consider the data

$$\theta=2, \quad \eta=3.$$

Fig. 1 shows that this value-pair lies in a region of stability. For any assumed value of ρ , L is calculated according to the following scheme :

$$\begin{array}{cccc} \frac{\theta}{(\rho+4)^2} & \frac{\theta}{(\rho+6)^2} & \frac{\theta}{(\rho+8)^2} & \dots\dots, \\ \frac{\theta}{(\rho+2)^2} & \frac{\theta}{(\rho+2)^2} \cdot \frac{\theta}{(\rho+4)^2} & \frac{\theta}{(\rho+4)^2} \cdot \frac{\theta}{(\rho+6)^2} & \frac{\theta}{(\rho+6)^2} \cdot \frac{\theta}{(\rho+8)^2} \dots\dots, \\ 1 - \frac{\eta}{(\rho+2)^2} & 1 - \frac{\eta}{(\rho+4)^2} & 1 - \frac{\eta}{(\rho+6)^2} & 1 - \frac{\eta}{(\rho+8)^2} \dots\dots, \\ \gamma_1 & \gamma_2 & \gamma_3 & \gamma_4 \dots\dots, \\ \phi_1 & \phi_2 & \phi_3 & \phi_4 \dots\dots, \end{array}$$

where

$$\gamma_r = \frac{\theta^2}{(\rho+2r)^2(\rho+2r+2)^2} \div \phi_{r+1},$$

$$\phi_r = 1 - \frac{\eta}{(\rho+2r)^2} - \gamma_r,$$

and finally

$$L = \frac{\theta}{(\rho+2)^2} \div \phi_1.$$

The number of significant figures required diminishes as the scheme proceeds to the right. The scheme stops at the n th column if γ_n does not affect the last figure in that column. Similarly R is calculated according to the similar scheme :

$$\begin{array}{cccc} \frac{\theta}{(\rho-4)^2} & \frac{\theta}{(\rho-6)^2} & \frac{\theta}{(\rho-8)^2} & \dots\dots\dots, \\ \frac{\theta}{(\rho-2)^2} & \frac{\theta}{(\rho-2)^2} \cdot \frac{\theta}{(\rho-4)^2} & \frac{\theta}{(\rho-4)^2} \cdot \frac{\theta}{(\rho-6)^2} & \frac{\theta}{(\rho-6)^2} \cdot \frac{\theta}{(\rho-8)^2} \dots\dots, \\ 1 - \frac{\eta}{(\rho-2)^2} & 1 - \frac{\eta}{(\rho-4)^2} & 1 - \frac{\eta}{(\rho-6)^2} & 1 - \frac{\eta}{(\rho-8)^2} \dots\dots, \\ \gamma_{-1} & \gamma_{-2} & \gamma_{-3} & \gamma_{-4} \dots\dots, \\ \phi_{-1} & \phi_{-2} & \phi_{-3} & \phi_{-4} \dots\dots, \end{array}$$

where

$$\gamma_{-r} = \frac{\theta^2}{(\rho - 2r)^2(\rho - 2r - 2)^2} \div \phi_{-r-1},$$

$$\phi_{-r} = 1 - \frac{\eta}{(\rho - 2r)^2} - \gamma_{-r},$$

and finally

$$R = \frac{\rho^2 - \eta}{\theta} - \frac{\theta}{(\rho - 2)^2} \div \phi_{-1}.$$

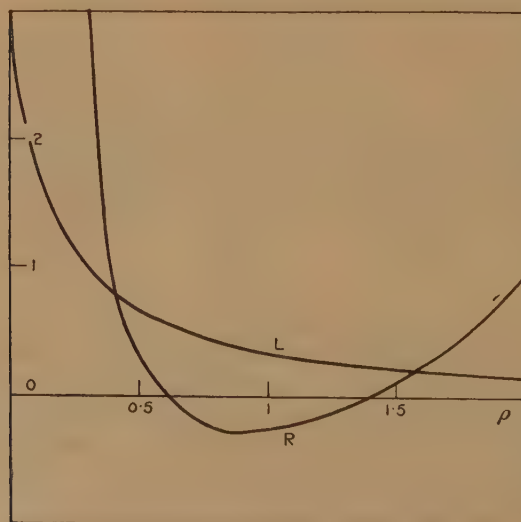
The method of procedure is as before.

As there was no indication as to the correct value of ρ , the following table was constructed :

ρ .	L.	R.
0.00	2.9010	-5.4011
0.25	1.1142	+5.1212
0.50	0.6630	+0.3065
0.75	0.4590	-0.2077
1.00	0.3438	-0.2559
1.25	0.2703	-0.1227
1.50	0.2197	+0.1157
1.75	0.1830	+0.4184
2.00	0.1553	+0.9457

The variation of L and R is illustrated in fig. 2.

Fig. 2.



Thus in the range considered there are two admissible values of ρ , whose sum is 2. The higher value is chosen to work with because the curves are flatter, and therefore interpolation is easier in its neighbourhood than in the neighbourhood of the other value.

By linear interpolation between $\rho=1.50$ and $\rho=1.75$ the value $\rho=1.5766$ is obtained. This gives

$$\rho=1.5766, \quad L=0.2072688, \quad R=0.2034813.$$

A second linear interpolation between $\rho=1.50$ and this value gives $\rho=1.5794$, leading to

$$\rho=1.5794, \quad L=0.2068352, \quad R=0.2067923.$$

Hence, if Δ denotes difference in the seventh decimal-place

$$\Delta\rho=28000, \quad \Delta L=-4336, \quad \Delta R=+33110.$$

Thus a more correct value of ρ is

$$\begin{aligned} \rho &= 1.5794 + \frac{L-R}{\Delta R - \Delta L} \Delta\rho \\ &= 1.579432. \end{aligned}$$

It has been remarked that the scheme of working gives not only the value of ρ to any desired degree of precision, but also the coefficients in the expansion of the solution. For this reason the figures in the scheme with the new value $\rho=1.579432$ will be given in full. The scheme for L reads as follows :

	·06424658	·03481422	·0217947	·01492
·156099712	·01002887	·00223670	·0007588	·000325
·765850432	·90363013	·9477787	·967308	·9776
11127511	236189	7847	333	—
·754722921	·90126824	·9469940	·966975	·9776

$$L = 0.20683049.$$

The scheme for R is :

	·341346474	·102346702	·04851578	·0282063	·0184
11·30726434	3·85969481	·034935685	·00496543	·0013685	·00052
—15·96089651	·487980289	·84647995	·9272263	·95769	·972
8·64539056	41534893	536341	14298	53	—
—24·60628707	·446445396	·84111654	·9257965	·95716	·972

$$\frac{\rho^2 - \eta}{\theta} = -0.25269728$$

$$- \frac{\theta}{(\rho - 2)^2} \div \phi_{-1} = 0.45952745$$

$$R = 0.20683017$$

Since L and R agree to the sixth place, ρ is correct to within a unit in the sixth place. A more precise value of ρ is

$$\begin{aligned}\rho &= 1.579432 + (L - R) \frac{\Delta \rho}{\Delta R - \Delta L} \\ &= 1.579432 + .00000032. \\ &= 1.57943227.\end{aligned}$$

The complementary value is

$$\rho = 0.42056773.$$

5. Determination of the Coefficients.

The coefficients will now be determined to six-place accuracy. Let $e_0 = 1$, then

$$\begin{aligned}e_1 &= -0.206830 ; \\ \frac{e_2}{e_1} &= -\frac{\theta}{(\rho + 4)^2} \div \phi_1 = -\frac{.0642466}{.901268} = -0.0712846, \\ e_2 &= +0.014744 ; \\ \frac{e_3}{e_2} &= -\frac{\theta}{(\rho + 6)^2} \div \phi_2 = -\frac{.034814}{.94699} = -0.036763, \\ e_3 &= -0.000542 ; \\ \frac{e_4}{e_3} &= -\frac{\theta}{(\rho + 8)^2} \div \phi_3 = -\frac{.0218}{.967} = -0.0225, \\ e_4 &= +0.000012.\end{aligned}$$

Similarly

$$\begin{aligned}\frac{e_{-1}}{e_0} &= -\frac{\theta}{(2 - \rho)^2} \div \phi_{-1} = \frac{11.307264}{24.606287} = +0.459527, \\ e_{-1} &= +0.459527 ; \\ \frac{e_{-2}}{e_{-1}} &= -\frac{\theta}{(4 - \rho)^2} \div \phi_{-2} = -\frac{.3413465}{.4464454} = -0.7645873, \\ e_{-2} &= -0.351349 ; \\ \frac{e_{-3}}{e_{-2}} &= -\frac{\theta}{(6 - \rho)^2} \div \phi_{-3} = -\frac{.102347}{.841117} = -0.121680, \\ e_{-3} &= +0.042752 ;\end{aligned}$$

$$\frac{e_{-4}}{e_{-3}} = -\frac{\theta}{(8-\rho)^2} \div \phi_{-4} = -\frac{.048516}{.92580} = -0.052404,$$

$$e_{-4} = -0.002240 ;$$

$$\frac{e_{-5}}{e_{-4}} = -\frac{\rho}{(10-\rho)^2} \div \phi_{-5} = -\frac{.02821}{.9572} = -0.0295,$$

$$e_{-5} = +0.000066 ;$$

$$\frac{e_{-6}}{e_{-5}} = -\frac{\theta}{(12-\rho)^2} \div \phi_{-6} = -\frac{.0184}{.972} = -0.019,$$

$$e_{-6} = -0.000001.$$

The first solution of the Mathieu equation,

$$\frac{d^2y}{dx^2} + (3 - 4 \cos 2x)y = 0,$$

is therefore to six-place accuracy :

$$\begin{aligned} y = & \cos 1.579432 x - 0.206830 \cos 3.579432 x \\ & + 0.014744 \cos 5.579432 x - 0.000542 \cos 7.579432 x \\ & + 0.000012 \cos 9.579432 x \\ & + 0.459527 \cos 0.420568 x - 0.351349 \cos 2.420568 x \\ & + 0.042752 \cos 4.420568 x - 0.002240 \cos 6.420568 x \\ & + 0.000066 \cos 8.420568 x - 0.000001 \cos 10.420568 x. \end{aligned}$$

The second solution is obtained by merely writing sine for cosine throughout.

6. Change of Sign of θ .

Fig. 1 is symmetrical about the η -axis, though it should be noted that in the negative half of the plane a_{2m+1} and b_{2m+1} are interchanged. Consequently, if the number-pair (θ, η) gives stability, so also does the number-pair $(-\theta, \eta)$. The Mathieu equation is unaltered if θ is replaced by $-\theta$ and x by $\frac{1}{2}\pi - x$, so if

$$y = A \sum_{-\infty}^{\infty} e_r \cos(2r + \rho)x + B \sum_{-\infty}^{\infty} e_r \sin(2r + \rho)x$$

is the general solution of (1), then the general solution of

$$\frac{d^2y}{dx^2} + (\eta + 2\theta \cos 2x)y = 0$$

is

$$y = A \sum_{-\infty}^{\infty} e_r \cos(2r + \rho)(\tfrac{1}{2}\pi - x) + B \sum_{-\infty}^{\infty} e_r \sin(2r + \rho)(\tfrac{1}{2}\pi - x) \\ = A_1 \sum_{-\infty}^{\infty} (-)^r e_r \cos(2r + \rho)x + B_1 \sum_{-\infty}^{\infty} (-)^r e_r \sin(2r + \rho)x,$$

where

$$A_1 = A \cos \tfrac{1}{2}\rho\pi + B \sin \tfrac{1}{2}\rho\pi, \quad B_1 = A \sin \tfrac{1}{2}\rho\pi - B \cos \tfrac{1}{2}\rho\pi.$$

Thus in general the only change in the fundamental solutions is a change in sign of the coefficients of odd rank. As before, the only exceptions arise when ρ is an integer or zero, in which cases A or B , and consequently A_1 or B_1 , are zero.

LIII. *On the Zeeman Resolution of the Oxygen Spectral Line at $\lambda 5577 \text{ \AA.}$, the Auroral Green Line.* By Prof. J. C. McLENNAN, *F.R.S.*, J. H. McLEOD, *M.A.**, and RICHARD RUEDY, *Ph.D.†*

[Plate VI.]

IN previous publications⁽¹⁾ it has been shown that the green spectral line of the aurora and of the light of the night sky originates in oxygen in the atomic form in the upper atmosphere. A problem still outstanding is to determine just what electronic transition represented in the spectral scheme for oxygen is responsible for the production of this radiation at $\lambda 5577 \text{ \AA.}$ A careful search for other spectral lines that might be associated with the green line has up to the present failed to elucidate the problem. A powerful method of classifying spectral lines is found in the character of the resolution experienced by the lines when the radiation giving rise to them is emitted by atoms in the presence of a magnetic field.

In 1927 McLennan, McLeod, and McQuarrie⁽²⁾ reported some visual observations on the Zeeman resolution of the oxygen green line in which it was seen that, viewed longitudinally, the green line was resolved into a doublet, the amount of whose separation appeared to be the same as that of the two outer components of a normal triplet.

* J. H. McLeod wishes to acknowledge his indebtedness to the Research Council of Canada for the grant of a Fellowship that enabled him to participate in this work.

† Communicated by the Authors.

The present paper deals with a more exact determination of the longitudinal Zeeman effect of the oxygen green line.

The necessary magnetic field was provided by a water-cooled solenoid shown diagrammatically in fig. 1. The coil was wound on a brass tube as shown, and consisted of ten layers of No. 16 B. & S. gauge enamelled single silk-covered copper wire. The layers were separated from each other by ebonite strips *F* each $\frac{1}{32}$ inch in thickness by $\frac{1}{8}$ inch in width, laid parallel to the axis of the coil and about 1 cm. from each other. These strips provided a series of open spaces running longitudinally to the coil between each layer of wire. The ebonite end-pieces *B* were perforated with many small holes to provide openings at each end of the spaces between the layers of the coil. When the coil was in operation tap water was forced through the spaces from one end of the coil to the other, so that every wire was bathed by flowing water. This method of cooling made it possible to pass a current of 30 amperes through the windings continuously, with a rise in temperature of the cooling water of only 9 or 10 degrees.

The length of the solenoid was 35 cm. and the total number of turns was 2390. The calculated field then for 30 amperes was 2620 gauss. Too much reliability should not be placed on this calculated value of the field for it could be that some current might leak through small cracks in the insulating enamel and so reduce the value of the field.

A comparison of the strength of the magnetic field at different points throughout the coil was made by means of a small search coil and a ballistic galvanometer. Fig 2 shows the graph obtained when deflexions of the galvanometer (proportional to the field strength) were plotted against distance through the solenoid. It is seen that for a distance of nearly 25 cm. in the central portion of the coil the field was within a few per cent. of being uniform. It was light emitted in the central portion of the solenoid that was used in the determination of the magnetic resolution of the green line.

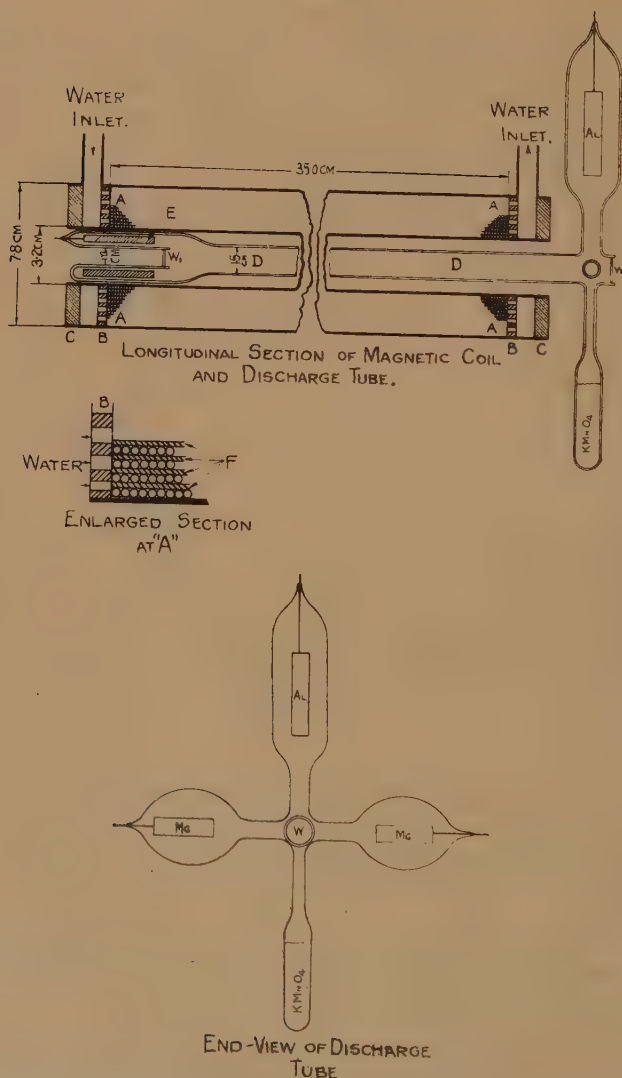
The green line radiation was produced in a tube containing a mixture of argon and oxygen. A current of about 30 m.a. from a 2000-volt D.C. motor-generator set was used to excite the tube.

A second tube containing neon gas was used to measure the strength of the magnetic field both before and after an exposure with the tube containing oxygen and argon was made. The yellow neon line at $\lambda 5852\text{\AA}$ was used as the standard.

560 Prof. McLennan, Mr. McLeod, and Dr. Ruedy :

Several conditions had to be fulfilled in the design of a suitable discharge-tube. It had to be designed so that it

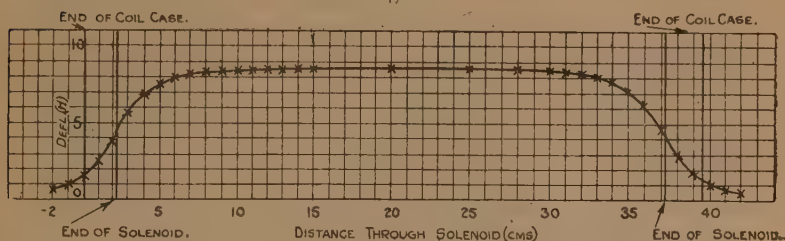
Fig. 1.



could be placed in or removed from the magnetic solenoid at will. In addition it had to be made so as to emit to the

resolving apparatus as much as possible of the light from that part of the tube which was in the uniform portion of the magnetic field and as little as possible from portions of the tube outside the field. At the same time no light was desired from the proximity of the electrodes. Fig. 1 shows the type of tube evolved to fulfil the conditions that have been enumerated above. By passing a heavy current between the magnesium electrodes shown it was possible to purify the gas to such a degree that the tube could be permanently sealed off from the pump and argon supply. A pair of aluminium electrodes was used to carry the existing current. By making one of them in the form of a cylinder and by placing it co-axially with the bore of the tube as shown at E it was possible to slide the discharge-tube into the solenoid to the position shown in fig. 1. Moreover, the discharge could be observed longitudinally through the hollow electrode. By having the window W_1

Fig. 2.



placed at the end of a re-entrant portion of the tube we were able to ensure that while light from the space in the tube in front of the window could pass out to the spectrograph, light from the space near the electrode was prevented from doing so. The tube and the solenoid were placed in the relative positions shown in fig. 1. A reference to fig. 2 will show that for a distance of about 25 cm. along the discharge-tube in front of the window W_1 the magnetic field was very nearly uniform. Farther along the discharge-tube than 25 cm. the magnetic field of course fell off in value, but that part of the tube was so far from the spectrograph that very little light from it could enter the spectrograph.

The resolving apparatus used consisted of a 45-plate echelon grating* with a constant deviation spectrograph to

* This instrument was presented to the Physical Laboratory of the University of Toronto by Messrs. Samuel and Benjamin of London and Toronto.

separate out the various spectral lines. The spectrograph slit and the edges of the echelon-plates were parallel and vertical. The constants of the echelon as given by the Adam Hilger Co., the makers, were as follows :—

Number of plates	45
Thickness of each plate	14.76 mm.
Width of step	1.0 mm.
Refractive indices :	

λ (I.A.).	μ .
6562.793	1.57185
5895.930 } 5889.963 }	1.5759
4861.327	1.58581
4307.908	1.59417

From these constants the value of $\Delta\lambda$ max., the portion of the spectrum included between consecutive orders of the same line, was calculated. The two values used were $\Delta\lambda$ max. for $\lambda 5577 \text{ \AA} = 0.336 \text{ \AA}$ and $\Delta\lambda$ max. for $\lambda 5852 \text{ (Ne)} = 0.376 \text{ \AA}$.

The echelon was adjusted to give two orders of equal intensity for the line being photographed. This adjustment made it possible to get a measure of the displacement on the plate corresponding to $\Delta\lambda$ max., with a much shorter exposure of the plate than would have been the case if the maximum intensity had been thrown into one order.

Three photographs of the Zeeman resolution of the oxygen green line were made. Before and after each of these exposures a photograph of the Zeeman resolution of the yellow neon line at $\lambda 5852 \text{ \AA}$ was taken in order to get a measure of the field strength. Pl. VI. fig. 1 shows a sample of a photograph of the Zeeman effect of the oxygen green line and Pl. VI. fig. 2 shows a similar one taken of the yellow neon line.

The duration of the exposure for the Zeeman effect of the green line was from 45 to 60 minutes and for the neon line it was from 4 to 8 minutes.

Back⁽³⁾ has shown that the neon line $\lambda 5852 \text{ \AA}$ has for its Zeeman pattern the following $\frac{(0) 31}{30}$. By a measurement on the photographs of the separation Δx of the Zeeman components of the neon line and by a measurement of Δx max. between the orders, it was possible by simple calculation for us, knowing $\Delta\lambda$ max., to determine the field-strength. Table I. gives the actual results obtained.

TABLE I.

	Δx max. mm.	Δx mm.	$\Delta \lambda$ max. A.	$\Delta \lambda$ experi- mental.	H calculated from Neon Gauss.	H mean.	Current amps.	$\Delta \lambda$ calcu- lated.	Ratio: $\frac{\Delta \lambda \text{ exper.}}{\Delta \lambda \text{ calc.}}$
Plates number one.	(Neon.....	λ 5852 A	0.649	0.153	0.376	0.0886	2660	30.0	
	{ Oxygen.....	λ 5577 A	0.624	0.132	0.336	0.0711	2720	30.0	0.895
	(Neon.....	λ 5852 A	0.658	0.162	0.376	0.0926	2780	30.0	
Plates number two.	(Neon.....	λ 5852 A	0.654	0.150	0.376	0.0863	2635	30.5	
	{ Oxygen.....	λ 5577 A	0.650	0.150	0.336	0.0774	2650	30.5	1.000
	(Neon.....	λ 5852 A	0.660	0.156	0.376	0.0888	2665	30.5	
Plates number three.	(Neon.....	λ 5852 A	0.661	0.165	0.376	0.0938	2810	30.0	
	{ Oxygen.....	λ 5577 A	0.662	0.148	0.336	0.0751	2690	30.0	0.957
	(Neon.....	λ 5852 A	0.703	0.160	0.376	0.0856	2570	30.0	
Mean.....									0.96

The column headed "H mean" gives in each case the mean value of the magnetic field from the values obtained before and after the green line Zeeman effect was photographed. The column headed " $\Delta\lambda$ calculated" gives the separations between the outer components of a normal triplet for the field values given in the previous column. Finally, the last column gives the ratio of the observed $\Delta\lambda$ to the calculated $\Delta\lambda$ for a normal triplet.

The mean of the three results gives the magnetic separation of the oxygen green line to be 0.96 of the normal amount.

The neon lines were rather fuzzy, as can be seen from Pl. VI. fig. 2, and consequently it was difficult to judge just where the maximum of the line occurred. The determination of the field strength was therefore subject to error. Though there is little doubt that the total experimental error could have been as much as 4 per cent., we had no hesitation in concluding that the Zeeman separation of the green line was normal. Since parallel components would be absent for longitudinal observation, we take it that the oxygen green line at λ 5577 Å is resolvable magnetically into a *normal triplet*.

From the result that the magnetic resolution of the green line is a normal triplet, it is possible to determine with a considerable amount of definiteness the exact location of the oxygen green line in the spectral scheme for atomic oxygen.

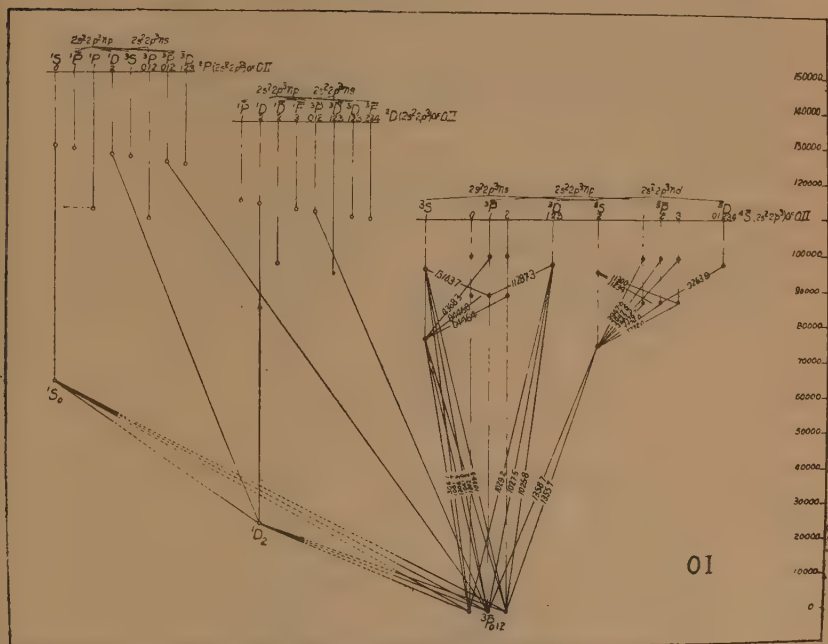
Fig. 3 is a diagram of this spectral scheme. It consists of three systems. Two of them have the metastable levels $^1S_0$ and $^1D_2$ for their lowest terms. The system with $^3\bar{P}_{012}$ as its lowest term is well known. Those with $^1S_0$ and $^1D_2$ as lowest terms, as well as the one based more immediately on the $^3\bar{P}_{012}$ term, are systems predicted on the basis of the Hund theory. There is no possible place for the green line in the scheme having $^3\bar{P}_{012}$ for its deepest level, so we must confine our attention to the other two schemes.

A brief consideration of the energy relations involved enables one to limit further the position of the green line in the spectral term scheme of oxygen. An examination of fig. 3 will show that two spectral lines occur in that region of the oxygen spectrum that could be most easily photographed, if radiation covering it were included in the light coming to us from the night sky. They are at λ 4368 Å and λ 3947 Å. No such lines, however, have ever been observed in the spectrum of the light from the night sky.

From this fact it may be concluded, therefore, that, under the conditions that give rise to the emission of radiation from the night sky corresponding to the auroral green line, there is not sufficient energy available to raise the oxygen in the upper atmosphere to the atomic levels involved in the production of the wave-lengths $\lambda 4368 \text{ \AA}$ and $\lambda 3947 \text{ \AA}$.

It follows from this that there cannot be sufficient energy available to permit of electronic transitions to the low $^3, ^1P$

Fig. 3.



In 1927 ⁽⁴⁾ the authors pointed out that it would be necessary to include so-called "forbidden" transactions in our considerations when seeking for a place for the green line in the spectral term scheme for atomic oxygen.

Moreover, Bowen ⁽⁵⁾ has since shown that a number of the nebulium spectral lines result from electronic transitions ordinarily classed as forbidden ones. This furnishes conclusive evidence that metastable states are not absolutely stable ones, and that they, too, are states of excitation from which spontaneous transitions accompanied by the emission of radiation can occur.

The predicted Zeeman effects of all the transitions originating in the lower metastable states of the oxygen atom are given in Table II.

TABLE II.

Transition,	Zeeman Pattern,
$^1S_0 \rightarrow ^1D_2$	$(0) \frac{1}{1}$.
$^1S_0 \rightarrow ^3P_0$	$\frac{0}{0}$.
$^1S_0 \rightarrow ^3P_1$	$(0) \frac{3}{2}$.
$^1S_0 \rightarrow ^3P_2$	$(0) \frac{3}{2}$.
$^1D_2 \rightarrow ^3P_0$	$(0) \frac{1}{1}$.
$^1D_2 \rightarrow ^3P_1$	$(0) \frac{(1) 1 2 3}{2}$.
$^1D_2 \rightarrow ^3P_2$	$(0) \frac{(1) (2) 1 2 3 4}{2}$.

It will be seen that two possible transitions could give rise to a normal triplet Zeeman effect. We may at once rule out the transition $^1D_2 \sim ^3P_0$ because if it were the transition that gave rise to the auroral green line the transitions $^1D_2 \sim ^3P_1$ and $^1D_2 \sim ^3P_2$ would certainly be present and would give rise to two spectral lines in the vicinity of $\lambda 5577 \text{ \AA}$. These have never been observed.

Therefore it is seen that the green line at $\lambda 5577, 341 \text{ \AA}$ in the spectrum of oxygen must have its origin in electronic transitions from $^1S_0$ metastable levels of oxygen atoms to $^1D_2$ ones.

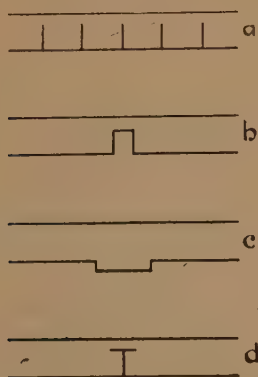
References.

- (1) McLennan & Shrum, Proc. Roy. Soc. A, cviii. p. 501 (1925).
McLennan, McLeod, and McQuarrie, Proc. Roy. Soc. A, cxiv. p. 1 (1927).
Cario, *Zeit. f. Physik*, xlii. p. 15 (1927).
McLennan and McLeod, Proc. Roy. Soc. A, cxv. p. 515 (1927).
- (2) McLennan, McLeod, and McQuarrie, Proc. Roy. Soc. A, cxiv. p. 1 (1927).
- (3) Back, *Ann. d. Physik*, lxxvi. p. 317 (1925).
- (4) McLennan, Ruedy, and McLeod, Trans. Roy. Soc. Canada, ser. iii. vol. xxi. section iii. (1927).
- (5) Bowen, 'Nature,' Oct. 1, 1927.

LIV. *The Effect on the Heat-flow through an Insulating Wall of Certain Modifications of Shape of its Isothermal Boundaries.* By F. H. SCHOFIELD, B.A., B.Sc.*

IN dealing with the steady flow of heat through a plane wall of insulating material, large in area in proportion to its thickness and with isothermal boundaries, it suffices

Fig. 1.



to treat the matter as one of two-dimensional flow between infinite parallel isothermals. It is proposed, on this basis, to investigate the effect on the heat-flow through such a wall due to certain modifications of one of its boundaries. The shapes dealt with are according to the sections shown in fig. 1. Of these (a) represents a series of thin projections, of equal depth and spacing, from one of the isothermals such

* Communicated by G. W. C. Kaye, Superintendent, Physics Department, National Physical Laboratory, Teddington, Middlesex.

as would correspond roughly to the metallic ribs of a ship projecting into a wall of insulation applied internally against its side; (*b*) and (*c*) represent single projections of finite width, respectively internal and external, such as would be encountered in a wall of insulation applied against a surface with either a projecting buttress or a recess; and (*d*) represents a single rib projection of T section. The solutions in these cases would, of course, apply where the modifications of one boundary are duplicated in the other as if by mirror reflexion about the mid-plane.

While the problems to be considered are thus stated in terms of heat-flow, it will readily be understood that they might equally well be expressed in relation to any other phenomenon which is subject to the Laplace equation. For example, the problems might be considered as those of the flow of electric current in long strips of metal of uniform thickness cut to the shapes indicated, or of the distribution of electrostatic charge and potential in the case of condensers of the appropriate cross-section extending to infinity in a plane perpendicular to that of the paper.

The method of solution employed is that of conformal representation, using the transformation found by Christoffel and Schwarz*.

I. A SERIES OF THIN RIBS.

In this case it is clear from considerations of symmetry that the flow lines from the tip of each rib, and from the points on the lower boundary, midway between the ribs, will be straight lines normal to the upper boundary. Hence it is only necessary to consider the rectangle formed by two such adjacent flow lines and the isothermal boundaries joining them. (See z plane, fig. 2.) This corresponds to the problem of the electrical resistance of a rectangular strip of metal with two electrodes supplied along the whole or portions of the sides—in the particular instance now under consideration the resistance of ABCD with electrodes along AD and BE—which has been treated generally by Moulton†. For our purpose it is convenient to follow a less general treatment than Moulton's and adopt the transformation shown in fig. 2. The linear dimensions l , m , and n of the z plane and l of the w plane are as indicated, while the

* For a discussion of this transformation with numerous examples, see J. J. Thomson's 'Recent Researches in Electricity and Magnetism,' chap. iii. (Clarendon Press, 1893.)

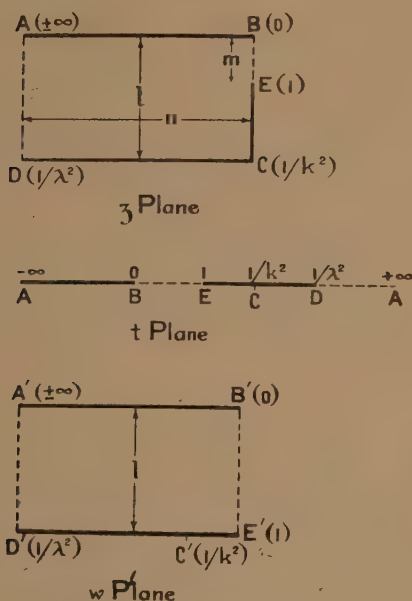
† Proceedings of London Mathematical Society, iii. p. 104 (1905). Also Jeans, 'Electricity and Magnetism,' 4th edition, p. 354.

lettering in brackets at the corners of the rectangles are the lengths along the real axis in the t plane, subject to the condition $\lambda < k < 1$. In fig. 2 and other similar diagrams the convention is adopted of showing the boundary isothermals and flow lines as full and dashed lines respectively.

The relation which converts the boundary ABCD, and the space inside it, into the real axis and upper half of the t plane, respectively is

$$dz/dt = Lt^{-\frac{1}{2}}(t-1/\lambda^2)^{-\frac{1}{2}}(t-1/k^2)^{-\frac{1}{2}}, \quad \dots \quad (1)$$

Fig. 2.



L being a constant. Putting $t = r^2/k^2$, we have

$$z = M \int \frac{dr}{\sqrt{1-r^2} \sqrt{1-r^2(\lambda^2/k^2)}} + N, \quad \dots \quad (2)$$

where M and N are constants. Calling B the origin and BC the real axis, N becomes zero, and we have

$$l = M \times K \pmod{\lambda/k}. \quad \dots \quad (3)$$

$$\text{and} \quad l/n = K, K' \pmod{\lambda/k}. \quad \dots \quad (4)$$

Hence combining (2) and (3) *,

$$z = (l/K) \operatorname{sn}^{-1}(k \sqrt{t}, \lambda/k), \quad \dots \quad (5)$$

and the length BE is given by

$$m = (l/K) \operatorname{sn}^{-1}(k, \lambda/k). \quad \dots \quad (6)$$

Similarly, the transformation from the w to the t plane yields

$$w = (l/K) \operatorname{sn}^{-1}(k \sqrt{t}, \lambda). \quad \dots \quad (7)$$

Hence from (5), (6), and (7),

$$\operatorname{sn}(Kz/l, \lambda/k) = k \sqrt{t} = \operatorname{sn}(Km/l, \lambda/k) \operatorname{sn}(Kw/l, \lambda). \quad (8)$$

The constants λ and k are known in terms of the dimensions l, m, n of the z plane through equations (4) and (6) above.

Hence the equation (8) gives the coordinates $(x+iy)$ of any point of the z plane in terms of the coordinates $(u+iv)$ of the corresponding point in the w plane, and so gives the distribution of flow lines and isothermals of the former plane in terms of the rectilinear distribution of the latter. The necessary calculation, involving the splitting of (8) into real and imaginary parts and solving for x and y , would be very laborious, and probably the simplest way of obtaining the z plane distribution would be to prepare two charts giving a series of orthogonal curves for constant values of p and of q in the relation †

$$P + iQ = \operatorname{sn}(p + iq),$$

and for the respective moduli λ and λ/k . Then the first chart would give P and Q for any desired values of u and v , and, after multiplying the former by the constant $\operatorname{sn}(Km/l, \lambda/k)$, the second chart would enable the values of Kx/l and Ky/l to be read off. It is not proposed to apply the method here, especially in view of the fact that the calculation of the distribution in the simpler case of a single rib in an infinite layer has been given by Lees ‡, and that, as will be shown below, this case gives a very close approximation to that of a series of ribs unless the gaps between them are comparatively small.

With regard to overall heat-loss, the flow across the strip of width l and length AB in the z plane is equal to the flow

* Since the function is to be inverted it is here written sn^{-1} in place of Legendre's F .

† See *e. g.* Dixon's 'Elliptic Functions.' Appendix A. (Macmillan & Co., 1894.)

‡ Proc. Phys. Soc. xxiii. p. 361 (1911).

across the strip of width l and length $A'B'$ in the w plane, where the flow is entirely normal. If there were no ribs such as EC in the z plane, the heat-flow from AB would also be normal, and hence we may regard the effect of inserting the ribs as equivalent to adding a length $2X$ per rib to the strip where X is given by

$$X = A'B' - AB = l \{ K'/K(\text{mod } \lambda) - K'/K(\text{mod } \lambda/k) \} . \quad (9)$$

From this equation we may readily deduce the "added length" for the marginal case of a single rib in an infinite layer. Thus putting $\lambda=0$ we have a zero modulus for both sets of elliptic functions, so that in each case $K=\pi/2$, and

$$K'(\text{mod } \lambda) = Lt_{\lambda=0}[\log(4/\lambda)]$$

and

$$K'(\text{mod } \lambda/k) = Lt_{\lambda=0}[\log(4k/\lambda)],$$

and from equation (6)

$$k = \sin(m\pi/2l).$$

Hence

$$\begin{aligned} X &= (2l/\pi) \log(1/k) \\ &= (2l/\pi) \log \operatorname{cosec}(m\pi/2l), \quad . \quad . \quad . \quad (10) \end{aligned}$$

which agrees with Lees's direct solution for this marginal case, while for the general equation (8) degenerates into

$$\sin(z\pi/2l) = \sin(m\pi/2l) \cdot \sin(w\pi/2l), \quad . \quad . \quad (11)$$

which is equivalent to Lees's equation.

The added length X for a series of ribs is calculated for known values of l , m , and n from equation (9) as follows:— From equation (4), using Legendre's Tables, we get the modulus λ/k : from (6) the argument k , and hence the other modulus λ . In the following table are set out the values of X/l for a series of values of n/l , taking the two cases where the depth of the rib ($l-m$) is respectively $\frac{3}{4}$ and $\frac{1}{2}$ of that of the layer.

It will be seen that in the two cases taken the error in the total heat transfer due to using the formula (10), applicable to the infinite case, becomes less than 1 per cent. when the semi-distance n between the ribs is slightly more than one-half of the thickness of the layer (see cols. 4 and 7 of Table I.). Hence in most practical cases each rib of a series, which may be of various depths and spacings, can be treated independently as a single rib in an infinitely long layer.

TABLE I.

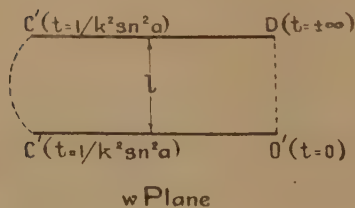
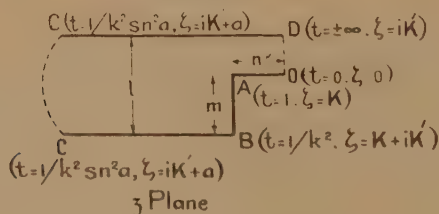
 $2X$ = the "Added Length" per rib.

n/l	$l=4m.$			$l=2m.$		
	X/l	Percentage diff. from ∞ case.		X/l	Percentage diff. from ∞ case.	
		$\frac{100(X_{\infty}-X)}{X}$	$\frac{100(X_{\infty}-X)}{n+X}$		$\frac{100(X_{\infty}-X)}{X}$	$\frac{100(X_{\infty}-X)}{n+X}$
Col. 1.	Col. 2.	Col. 3.	Col. 4.	Col. 5.	Col. 6.	Col. 7.
0.333	0.5070	20.6	12.4	0.1834	20.2	7.2
0.5	0.5731	6.7	3.6	0.2070	6.6	1.9
1	0.6098	0.3	0.1	0.2201	0.2	0.1
2	0.6116	0	0	0.2205	0	0
3	0.6120	0	0	0.2208	0	0
∞	0.6115	0	0	0.2206	0	0

II. THICK RIB OR BUTTRESS.

The diagram of this case is given in fig. 3 in the z and w

Fig. 3.



planes only, using the same conventions as before, but with a curved dotted line to indicate the flow line CC , which is

entirely at infinity. The transformation from the z to the t plane involves the third type of elliptic integral, and, with a view to obtaining the Jacobian form, we note that the infinity point C in the z plane gives rise to a term of the form $(t-b)^{-1}$ in the transformation. Hence b is conveniently put equal to $1/k^2 \operatorname{sn}^2 a$, while t is replaced by a new variable $\operatorname{sn}^2 \zeta$. Following a similar plan to that adopted in the previous case, the other corners of the polygon conveniently become as shown in the diagram, and the required transformation is given by

$$dz/dt = A(t-1)^{+\frac{1}{2}}(t-1/k^2 \operatorname{sn}^2 a)^{-1} t^{-\frac{1}{2}}(t-1/k^2)^{-\frac{1}{2}}. \quad (14)$$

Putting $t = \operatorname{sn}^2 \zeta$, and $M = -2Ak^3 \operatorname{sn}^2 a$, we obtain

$$\begin{aligned} \frac{dz}{d\zeta} &= M \left\{ \frac{\operatorname{cn}^2 \zeta}{1 - k^2 \operatorname{sn}^2 a \operatorname{cn}^2 \zeta} \right\} \\ &= M \left\{ 1 - \frac{\operatorname{dn}^2 a \operatorname{sn}^2 \zeta}{1 - k^2 \operatorname{sn}^2 a \operatorname{sn}^2 \zeta} \right\} \\ &= \frac{M}{k^2} \left\{ k^2 - \frac{\operatorname{dn} a}{\operatorname{sn} a \operatorname{cn} a} \left(\frac{k^2 \operatorname{sn} a \operatorname{cn} a \operatorname{dn} a \operatorname{sn}^2 \zeta}{1 - k^2 \operatorname{sn}^2 a \operatorname{sn}^2 \zeta} \right) \right\} \\ \therefore z &= \frac{M}{k^2} \left\{ k^2 \zeta - \frac{\operatorname{dn} a}{\operatorname{sn} a \operatorname{cn} a} \Pi(\zeta, a) \right\}. \quad (15) \end{aligned}$$

No integration constant is required if the origin is fixed at 0, the real axis being OA . The values of the new variable ζ at the corners of the polygon are as shown in fig. 3, and, in order to obtain the finite dimensions l, m, n in the z plane, we proceed as follows:— l is the change in z as t passes through $1/k^2 \operatorname{sn}^2 a$ (or ζ passes through $iK' + a$), and is therefore given by

$$il = i \frac{\pi M \operatorname{dn} a}{2k^2 \operatorname{sn} a \operatorname{cn} a}, \quad (16)$$

This expression may also be obtained by use of (18), (19), and (20) below. Substituting in (15), we have

$$z = \frac{2l}{\pi} \left\{ \frac{k^2 \operatorname{sn} a \operatorname{cn} a}{\operatorname{dn} a} \zeta - \Pi(\zeta, a) \right\}. \quad (17)$$

To obtain the other dimensions in the z plane, use is made of the following relations of the Π function:—

$$\Pi(K, a) = KZ(a). \quad (18)$$

$$\Pi(K + iK', a) = KZ(a) + i\{K'Z(a) + a\pi/2K\}. \quad (19)$$

$$\Pi(iK', a) = i\{K'Z(a) + a\pi/2K \pm \pi/2\}. \quad (20)$$

Hence from (17), (18), and (19),

$$\frac{n}{l} = \frac{2K}{\pi} \left\{ \frac{k^2 \operatorname{sn} a \operatorname{cn} a}{\operatorname{dn} a} - Z(a) \right\} \dots \dots \dots (21)$$

$$-\frac{m}{l} = \frac{2K'}{\pi} \left\{ \frac{k^2 \operatorname{sn} a \operatorname{cn} a}{\operatorname{dn} a} - Z(a) \right\} - \frac{a}{K}, \quad \dots \dots \dots (22)$$

the signs in (22) being consistent with (16), (19), and (20).

The length BC is infinite by virtue of the value of $\Pi(iK' + a, a)$, and since we propose to obtain the difference between this length and a corresponding infinite length in the w plane, we analyse the function by means of the addition theorem, as follows:—

$$\begin{aligned} \Pi(iK' + a, a) &= \operatorname{Lt}_{\epsilon=0} [\Pi(iK' + \epsilon + a, a)] \\ &= \operatorname{Lt}_{\epsilon=0} \left[\Pi(a, a) + \Pi(iK' + \epsilon, a) \right. \\ &\quad \left. + \frac{1}{2} \log \left\{ \frac{1 + \frac{k^2 \operatorname{sn} a \operatorname{sn} a}{k^2 \operatorname{sn} \epsilon \operatorname{sn} (2a + \epsilon)}}{1 - \frac{k^2 \operatorname{sn} a \operatorname{sn} a}{k^2 \operatorname{sn} \epsilon \operatorname{sn} \epsilon}} \right\} \right] \\ &= \Pi(a, a) + i\{K'Z(a) + a\pi/2K\} \\ &\quad - \frac{1}{2} \log \operatorname{sn} 2a + \operatorname{Lt}_{\epsilon=0} \left[\frac{1}{2} \log \operatorname{sn} \epsilon \right]. \quad (23) \end{aligned}$$

Hence BC is given by

$$\begin{aligned} BC &= OA + AB + BC - (OA + AB) \\ &= \frac{2l}{\pi} \left\{ \frac{k^2 \operatorname{sn} a \operatorname{cn} a}{\operatorname{dn} a} (a - K) + KZ(a) - \Pi(a, a) \right. \\ &\quad \left. + \frac{1}{2} \log \operatorname{sn} 2a - \operatorname{Lt}_{\epsilon=0} \left(\frac{1}{2} \log \operatorname{sn} \epsilon \right) \right\} \dots \dots \dots (24) \end{aligned}$$

Converting to the Θ function by the relation

$$\Pi(a, a) = aZ(a) - \frac{1}{2} \log \frac{\Theta(2a)}{\Theta(0)},$$

and combining with equation (21), we obtain

$$\begin{aligned} BC &= \frac{l}{\pi} \log \left\{ \frac{\operatorname{sn} 2a \Theta(2a)}{\Theta(0)} \right\} - n \left(1 - \frac{a}{K} \right) \\ &\quad - \frac{l}{\pi} \operatorname{Lt}_{\epsilon=0} (\log \operatorname{sn} \epsilon) \dots \dots \dots (25) \end{aligned}$$

This expression is infinite by virtue of the last term.

Turning now to the transformation which converts the w into the t plane, we have

$$dw/dt = t^{-1/2}(t - 1/k^2 \operatorname{sn}^2 a)^{-1}, \quad \dots \quad (26)$$

which yields on integration, for an origin O' and a real axis $O'C'$,

$$w = P \log \left\{ \frac{1 + k \operatorname{sn} a \sqrt{t}}{1 - k \operatorname{sn} a \sqrt{t}} \right\}, \quad \dots \quad (27)$$

the value of P being given by

$$il = P \log(-1) = P i \pi.$$

To obtain the length $O'C'$, we proceed in a similar way to that adopted in the case of the z plane, putting t equal to $1/k^2 \operatorname{sn}^2(a + \epsilon)$ and taking the limit for $\epsilon = 0$.

Thus

$$\begin{aligned} O'C' &= \lim_{\epsilon \rightarrow 0} \left[\frac{l}{\pi} \log \left\{ \frac{\operatorname{sn}(a + \epsilon) + \operatorname{sn} a}{\operatorname{sn}(a + \epsilon) - \operatorname{sn} a} \right\} \right] \\ &= \lim_{\epsilon \rightarrow 0} \left[\frac{l}{\pi} \log \left\{ \frac{\operatorname{sn} a \operatorname{cn} \epsilon \operatorname{dn} \epsilon + \operatorname{sn} \epsilon \operatorname{cn} a \operatorname{dn} a +}{\operatorname{sn} a \operatorname{cn} \epsilon \operatorname{dn} \epsilon + \operatorname{sn} \epsilon \operatorname{cn} a \operatorname{dn} a -} \right. \right. \\ &\quad \left. \left. \frac{+ \operatorname{sn} a (1 - k^2 \operatorname{sn}^2 \epsilon \operatorname{sn}^2 a)}{- \operatorname{sn} a (1 - k^2 \operatorname{sn}^2 \epsilon \operatorname{sn}^2 a)} \right\} \right] \\ &= \frac{l}{\pi} \log \frac{2 \operatorname{sn} a}{\operatorname{cn} a \operatorname{dn} a} - \frac{l}{\pi} \lim_{\epsilon \rightarrow 0} \{ \log \operatorname{sn} \epsilon \} \quad \dots \quad (28) \end{aligned}$$

The last term of this equation is infinite and identical with the last term of (25).

Now, if the heat-flow from $OA + AB + BC$ had been "normal," that is to say, perpendicular to OA and BC , it would have been equivalent to that across a strip of width l and of length $BC + OA(l/l - m)$. Actually the heat-flow in question is equal to the normal flow across a strip of width l and of length $O'C'$, since this is the length in the w plane, where the flow is entirely normal, equivalent to $OA + AB + BC$ in the z plane. Hence the excess of the actual heat-flow from $OA + AB + BC$ over the hypothetical normal flow is equivalent to the addition to the strip of width l of a length X given by

$$\begin{aligned} X &= O'C' - BC - OA(l/l - m) \\ &= \frac{l}{\pi} \log \left\{ \frac{2 \operatorname{sn} a \Theta(0)}{\operatorname{cn} a \operatorname{dn} a \operatorname{sn} 2a \Theta(2a)} \right\} \\ &\quad + n \left(1 - \frac{a}{K} \right) - n \left(\frac{l}{l - m} \right). \quad \dots \quad (29) \end{aligned}$$

This equation, together with (21) and (22), which determine the constants k and a in terms of the dimensions l , m , and n of the z plane, gives the solution of the "added length" in the case under consideration.

It is useful to check the result by degenerating the solution to obtain known marginal cases involving two finite dimensions. Thus:—

Case 1: $n/l=0$.

This is obtained by making the modulus k equal to zero, for then

$$K=\pi/2 \quad \text{and} \quad K'=Lt_{k=0}[\log(4/k)].$$

Hence from equation (21), noting that $Z(a)=0$, we have

$$n/l=0,$$

while from (22), noting that k^2 is the lowest power of k in $Z(a)$ and that in the limit $k^2 \log k$ is zero,

$$\begin{aligned} -\frac{m}{l} &= \frac{2}{\pi} \log\left(\frac{4}{k}\right) \{k^2 \sin a \cos a - Z(a)\} - \frac{2a}{\pi} \\ &= -\frac{2a}{\pi}. \end{aligned}$$

Hence since $\Theta(2a)/\Theta(0)=1$, we have

$$\begin{aligned} X &= \frac{l}{\pi} \log\left(\frac{2 \sin a}{\cos a \sin 2a}\right) \\ &= \frac{2l}{\pi} \log \sec\left(\frac{m\pi}{2l}\right), \quad \dots \dots \dots (30) \end{aligned}$$

which agrees with (10) above, allowing for the fact that m of the last-mentioned equation is here replaced by $l-m$.

Case 2: $m/l=0$.

This is obtained by putting $k=1$. Then since $\operatorname{cn} a = \operatorname{dn} a = \operatorname{sech} a$ and $\operatorname{sn} a = Z(a) = \tanh a^*$, and, as will be shown below, $\Theta(2a)/\Theta(0) = \cosh 2a$, we have $m/l=0$ and $X/l=0$.

Case 3: $nl=\infty$.

This is obtained by putting $k=1$ and $a=K-\beta$, where β is a finite quantity, K of course being infinite. For the purpose of equations (21) and (22), we note that

$$\begin{aligned} \frac{\operatorname{sn}(K-\beta) \operatorname{cn}(K-\beta)}{\operatorname{dn}(K-\beta)} &= \frac{\operatorname{sn} \beta \operatorname{cn} \beta}{\operatorname{dn} \beta} = \tanh \beta, \\ Z(K-\beta) &= \beta/K = 0. \end{aligned}$$

* For these degenerations and those used in obtaining equation (30), see *e. g.* Dixon's 'Elliptic Functions,' chap. viii. (Macmillan & Co.)

So that

$$\frac{n}{l} = \frac{2K}{\pi} (\tanh \beta - \beta/K) = \infty \quad (31)$$

$$-\frac{m}{l} = \tanh \beta - 1 \quad (32)$$

From the latter equation

$$\tanh \beta = (l-m)/l \quad \text{or} \quad \beta = \frac{1}{2} \log \frac{2l-m}{m} \quad (33)$$

For the purpose of dealing with equation (29), we have

$$\frac{\Theta(2a)}{\Theta(0)} = \frac{\Theta(2\beta)}{\Theta(0)} = e^{-\beta^2/2K + \int_0^{2\beta} \tanh x \, dx} = e^{\log \cosh 2\beta} = \cosh 2\beta \quad (34)$$

$$\begin{aligned} \log \left\{ \frac{2 \operatorname{sn}(K-\beta) \Theta(0)}{\operatorname{cn}(K-\beta) \operatorname{dn}(K-\beta) \operatorname{sn}(2K-2\beta) \Theta(2K-2\beta)} \right\} \\ = \log \left\{ \frac{2 \operatorname{cn} \beta \operatorname{dn} \beta \Theta(0)}{k'^2 \operatorname{sn} \beta \operatorname{sn} 2\beta \Theta(2\beta)} \right\} \\ = 2 \log \frac{4}{k'} + 2 \log \frac{1}{2 \sinh 2\beta} \quad (35) \end{aligned}$$

$$\begin{aligned} \frac{n}{l} \left(1 - \frac{a}{K} \right) - \frac{n}{l-m} &= \frac{n}{l} \left(\frac{\beta}{K} - \frac{1}{\tanh \beta} \right) \\ &= \frac{2\beta}{\pi} (\tanh \beta + \coth \beta) - \frac{2K}{\pi} \quad (36) \end{aligned}$$

Using the last two equations, we have from (29)

$$\frac{X}{l} = \frac{2}{\pi} \log \frac{m(2l-m)}{4l(l-m)} + \frac{1}{\pi} \left(\frac{l}{l-m} + \frac{-m}{l} \right) \log \frac{2l-m}{m} \quad (37)$$

Putting $m = (l-b)$, this becomes

$$\frac{X}{l} = \frac{1}{\pi} \left\{ 2 \log \frac{l^2 - b^2}{4lb} + \frac{l^2 + b^2}{lb} \log \frac{l+b}{l-b} \right\}, \quad (38)$$

which is identical with Lees's* direct solution for this marginal case.

Calculation of "Added Length."

The calculation of the "added length" in any particular case can be carried out by means of the Tables of Θ and

* Phil. Mag. xvi. p. 734 (1908).

allied functions due to Greenhill and Hippisley*. The functions are given for a series of values of the modulus k —for the most part for every 5° —and for every ninetieth part of K for the variable a . Expressed in terms of the notation used in the Tables, the variable r being equal to $90a/K$, equations 21, 22, and 29 become respectively

$$\frac{n}{l} = \frac{2K}{\pi} \left\{ \frac{k^2 A(r) B(r)}{k' C(r) D(r)} - E(r) \right\}. \quad (39)$$

$$\frac{m}{l} = \frac{r}{90} - \frac{2K'}{\pi} \left\{ \frac{k^2 A(r) B(r)}{k' C(r) D(r)} - E(r) \right\}. \quad (40)$$

$$\frac{X}{l} = \frac{1}{\pi} \log \left\{ \frac{2A(r) D(r)}{\sqrt{k' B(r) C(r) A(2r)}} \right\} + \frac{n}{l} \left(1 - \frac{r}{90} \right) - \frac{n}{l-m}. \quad (41)$$

When $2r$ is greater than 90° , it can be shown that $A(2r)$ in equation (41) should be replaced by $B(s)$, where s is equal to $(2r-90)$.

The plan adopted in the present case is to take a constant depth m of the buttress, and obtain the values of X for a series of values of n . For this purpose, taking any modulus k , the value of r is found by trial giving the required ratio m/l , and using this value of r , the ratios of n/l and X/l are readily calculated. Curves have been obtained as above described for two values of m/l , namely $\frac{1}{2}$ and $\frac{3}{4}$, and are shown in fig. 4, which gives the calculated points and the appropriate modular angles. It will be observed from the curves, marked $B(\frac{3}{4})$ and $B(\frac{1}{2})$, that the asymptotic approach to the final value is extremely rapid.

III. RECESS.

The transformation from the t to the w plane is the same as for the previous case, while that for the z plane is identical with that employed by Carter† in dealing with a problem in magnetism illustrated below in fig. 9. Following the practice in the previous cases, we shall however adopt the slight modification of cutting the figure into two parts by the central flow line (see fig. 5), and hence obtain the following equation for the transformation from the z to the t plane.

$$dz'_j dt = A t^{-\frac{1}{2}} (t-1)^{-\frac{1}{2}} (t-1/k^2)^{\frac{1}{2}} (t-1/k^2 \sin^2 a)^{-1}. \quad (42)$$

* 'Smithsonian Mathematical Formulæ and Tables of Elliptic Functions' (Publication No. 2672, Washington, 1922).

† Journ. Inst. Elect. Eng. vol. lxiv. p. 1117 (1926).

Fig. 4.

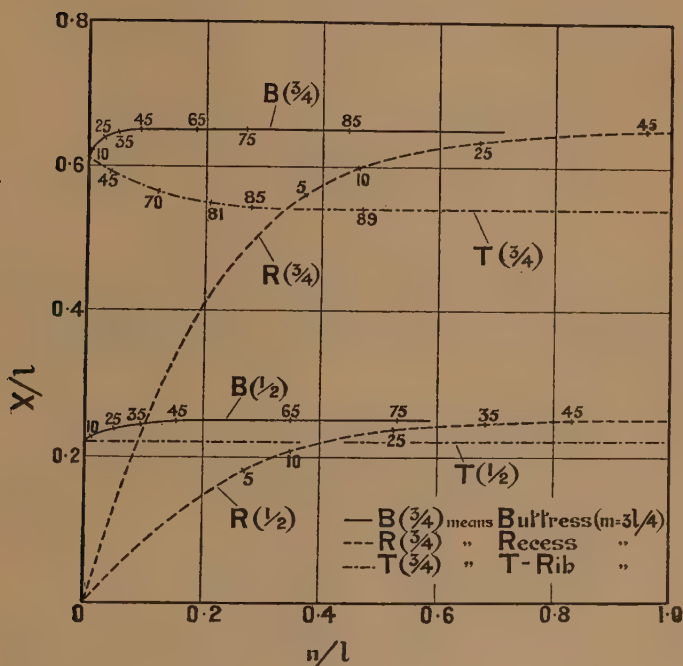
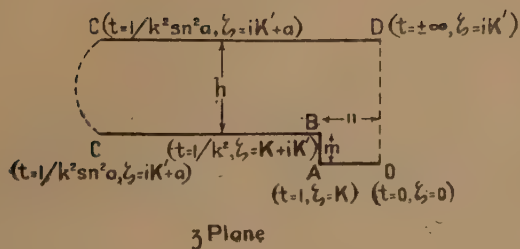


Fig. 5.



Putting $t = \operatorname{sn}^2 \zeta$ and $M = -2A k \operatorname{sn}^2 a$, we have, on integration, O being the origin and OA the real axis,

$$z = M \left\{ \zeta - \frac{\operatorname{cn} a}{\operatorname{sn} a \operatorname{dn} a} \Pi(\zeta, a) \right\}, \quad \dots \quad (43)$$

and for the finite dimensions h, m, n ,

$$h = \frac{M \operatorname{cn} a \pi}{2 \operatorname{sn} a \operatorname{dn} a} \quad \dots \quad (44)$$

$$\frac{m}{h} = \frac{2K'}{\pi} \left\{ \frac{\operatorname{sn} a \operatorname{dn} a}{\operatorname{cn} a} - Z(a) \right\} - \frac{a}{K} \quad \dots \quad (45)$$

$$\frac{n}{h} = \frac{2K}{\pi} \left\{ \frac{\operatorname{sn} a \operatorname{dn} a}{\operatorname{cn} a} - Z(a) \right\} \quad \dots \quad (46)$$

The expressions (44), (45), (46) agree with those given by Carter, but the remainder of the problem differs from that treated by him.

From (43) and (44) we have

$$z = \frac{2h}{\pi} \left\{ \frac{\operatorname{sn} a \operatorname{dn} a}{\operatorname{cn} a} \zeta - \Pi(\zeta, a) \right\}; \quad \dots \quad (47)$$

and hence using (23), (24), and (46),

$$\begin{aligned} BC &= \frac{2h}{\pi} \left\{ \frac{\operatorname{sn} a \operatorname{dn} a}{\operatorname{cn} a} (a - K) - (a - K) Z(a) \right. \\ &\quad \left. + \frac{1}{2} \log \frac{\operatorname{sn} 2a \Theta(2a)}{\Theta(0)} - \operatorname{Lt}_{\epsilon=0} \left(\frac{1}{2} \log \operatorname{sn} \epsilon \right) \right\} \\ &= \frac{h}{\pi} \log \frac{\operatorname{sn} 2a \Theta(2a)}{\Theta(0)} - n \left(1 - \frac{a}{K} \right) - \frac{l}{\pi} \operatorname{Lt}_{\epsilon=0} (\log \operatorname{sn} \epsilon). \end{aligned}$$

And since the length O'C' is given by (28), we have for the "added length" X

$$\begin{aligned} X &= O'C' - BC - OA(h/h + m) \\ &= \frac{h}{\pi} \log \left\{ \frac{2 \operatorname{sn} a \Theta(0)}{\operatorname{cn} a \operatorname{dn} a \operatorname{sn} a \Theta(2a)} \right\} + n \left(1 - \frac{a}{K} \right) - \frac{nh}{h+m}. \quad (49) \end{aligned}$$

The solution given by equations (45), (46), and (49) may be checked, as before, by degeneration into marginal cases, thus:—

Case 1: $m/h = 0$.

This is obtained by putting $k = 1$, in which case X can be shown to be zero.

Case 2: $m/h = \infty$.

This is obtained by putting $k = 0$, which gives

$$\frac{n}{h} = \tan a, \quad \frac{m}{h} = \infty.$$

$$\begin{aligned} X_1 &= \frac{h}{\pi} \log \left(\frac{2 \sin a}{\cos a} \frac{2 \sin a}{2 \sin a \cos a} \right) + n \left(1 - \frac{2a}{\pi} \right) \\ &= \frac{h}{\pi} \log \left(\frac{h^2 + n^2}{h^2} \right) + \frac{2n}{\pi} \left(\frac{\pi}{2} - \tan^{-1} \frac{n}{h} \right) \\ &= \frac{h}{\pi} \log \left(\frac{h^2 + n^2}{h^2} \right) + \frac{2n}{\pi} \tan^{-1} \frac{h}{n}, \quad \dots \quad (50) \end{aligned}$$

which is equivalent to J. J. Thomson's* solution for this marginal case. It is to be noted that when $n = 0$, X becomes zero, as would be expected.

Case 3: $n/h = \infty$.

This is obtained by putting $k = 1$ and $a = K - \beta$, where β is a finite quantity, K of course being infinite. Following the procedure previously adopted, equation (49) degenerates into Lees's marginal case, *i. e.* equation (37) above.

Calculation of "Added Length."

The calculation in this case was carried out in the manner already described. In order to get a comparison with the previous case, which is of course identical with it when n is infinite, l is substituted for $(h + m)$, and curves calculated for the same values of m as before, namely $l/2$ and $3l/4$. The curves (see fig. 4) start from zero and approach their final value when n/l is of the order of unity.

IV. T-SHAPED RIB.

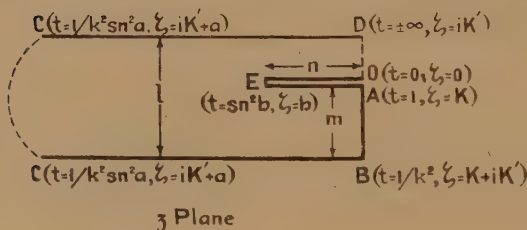
The w -plane diagram is identical with that used for the two preceding cases. The diagram in the z plane is as shown in fig. 6. Since we are concerned with both the upper and lower surfaces of OEA, these are shown separately for purposes of clearness, though, in fact, the projection OEA is infinitely thin. The third type of elliptic integral is again involved in the transformation from the z to the t plane, and hence the same sequence of descending values is adopted, as

* *Loc. cit.* p. 235.

before, for the points C, B, and A, namely $1/k^2 \operatorname{sn}^2 a$, $1/k^2$, and 1. Since it is not permissible to fix more than two absolute lengths along the axis in the t plane, or the ratios of three lengths, an arbitrary value has to be assigned to the point E, which must then be determined in relation to the constants k and a . The value at E must be less than 1, and, since the variable is to be changed to $\operatorname{sn}^2 \zeta$, the value in question is put equal to $\operatorname{sn}^2 b$. The required transformation is then

$$dz/dt = A(t - \operatorname{sn}^2 b)t^{-\frac{1}{2}}(t-1)^{-\frac{1}{2}}(t-1/k^2)^{-\frac{1}{2}}(t-1/k^2 \operatorname{sn}^2 a)^{-1}. \quad (51)$$

Fig. 6.



Putting $t = \operatorname{sn}^2 \zeta$ and $N = 2A k^3 \operatorname{sn}^2 a$, this yields on integration

$$z = N \left\{ \zeta \operatorname{sn}^2 b - \frac{1 - k^2 \operatorname{sn}^2 a \operatorname{sn}^2 b}{k^2 \operatorname{sn} a \operatorname{cn} a \operatorname{dn} a} \Pi(\zeta, a) \right\}, \quad (52)$$

no integration constant being required for the origin a and a real axis OE .

The points O and A being coincident in the z plan have, on putting $\zeta = K$,

$$0 = N \left\{ K \operatorname{sn}^2 b - K Z(a) \left(\frac{1 - k^2 \operatorname{sn}^2 a \operatorname{sn}^2 b}{k^2 \operatorname{sn} a \operatorname{cn} a \operatorname{dn} a} \right) \right\}.$$

$$\therefore \operatorname{sn}^2 b = \frac{Z(a)}{k^2 \operatorname{sn} a \operatorname{cn} a \operatorname{dn} a + k^2 \operatorname{sn}^2 a Z(a)}, \quad (53)$$

which gives the constant b in terms of a and k .

Then, since

$$l = N \frac{\pi}{2} \left\{ \frac{1 - k^2 \operatorname{sn}^2 a \operatorname{sn}^2 b}{k^2 \operatorname{sn} a \operatorname{cn} a \operatorname{dn} a} \right\}, \quad (54)$$

equation (52) may be written

$$\begin{aligned} z &= \frac{2l}{\pi} \left\{ \xi \frac{\operatorname{sn}^2 b (k^2 \operatorname{sn} a \operatorname{cn} a \operatorname{dn} a)}{1 - k^2 \operatorname{sn}^2 a \operatorname{sn}^2 b} - \Pi(\xi, a) \right\} \\ &= \frac{2l}{\pi} \{ \xi Z(a) - \Pi(\xi, a) \} \\ &= \frac{l}{\pi} \log \frac{\Theta(\xi + a)}{\Theta(\xi - a)}. \quad \dots \dots \dots (55) \end{aligned}$$

And for the finite dimensions m and n we have

$$\frac{m}{l} = \frac{a}{K}. \quad \dots \dots \dots (56)$$

$$\frac{n}{l} = \frac{1}{\pi} \log \frac{\Theta(b+a)}{\Theta(b-a)}. \quad \dots \dots \dots (57)$$

Further, we have

$$BC = \frac{l}{\pi} \left\{ \log \frac{\operatorname{sn} 2a \Theta(2a)}{\Theta(0)} - \lim_{\epsilon \rightarrow 0} (\log \operatorname{sn} \epsilon) \right\}; \quad (58)$$

so that the "added length," X , is given by

$$\begin{aligned} X &= O'C' - (BC - OE) - OE(l/l - m) \\ &= \frac{l}{\pi} \log \left\{ \frac{2 \operatorname{sn} a \Theta(0)}{\operatorname{cn} a \operatorname{dn} a \operatorname{sn} 2a \Theta(2a)} \right\} - \frac{nm}{l-m}. \quad (59) \end{aligned}$$

The marginal cases of $n/l = 0$ and $n/l = \infty$ are dealt with below.

Case 1: $n/l = 0$.

This is obtained by putting $k = 0$, and equation (59) readily reduces to (30).

Case 2: $n/l = \infty$. ("Added Length" and Distribution.)

This marginal case does not appear to have been dealt with elsewhere, so that an independent derivation of the expression for the "added length" is given together with a computation of the flow line and isothermal distribution for one particular case ($m = 3l/4$). This calculated distribution, applying when $n/l = \infty$, allows an approximate idea to be formed of that applicable to a finite value of n , even when the latter is quite small, and is therefore useful in showing the nature of the flow in the neighbourhood of the sharp edge.

Referring to fig. 7, we have for the transformations to the t -plane from the z and w planes

$$dz/dt = Pt(t-1)^{-1}(t+\bar{a})^{-1} \quad \dots \quad (60)$$

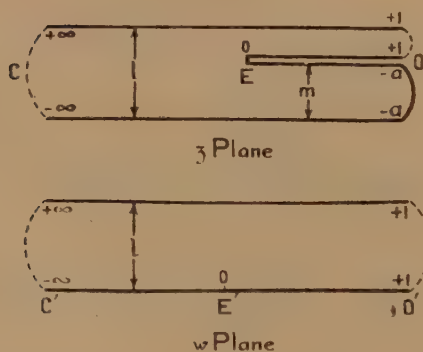
$$dw/dt = Q(t-1)^{-1} \quad \dots \quad (61)$$

Then, if E, E' and OC, O'U' are the respective origins and real axes, we have on integration and evaluation of the constants

$$w = \frac{l}{\pi} \log(1-t), \quad \dots \quad (62)$$

$$z = \frac{l-m}{\pi} \log(1-t) + \frac{m}{\pi} \log\left(1 + \frac{t}{a}\right), \quad \dots \quad (63)$$

Fig. 7.



where a is equal to $m/(l-m)$. Whence

$$EO = -\frac{l-m}{\pi} [\log(1-t)]_{t=1} - \frac{m}{\pi} \log\left(\frac{1+a}{a}\right). \quad (64)$$

$$EC = \frac{l}{\pi} [\log t]_{t=\infty} - \frac{m}{\pi} \log a. \quad \dots \quad (65)$$

$$E'O' = -\frac{l}{\pi} [\log(1-t)]_{t=1} \quad \dots \quad (66)$$

$$E'C' = \frac{l}{\pi} [\log t]_{t=\infty}. \quad \dots \quad (67)$$

$$\therefore X = O'E' + E'C' - EC - EO(l/l-m)$$

$$= \frac{lm}{(l-m)\pi} \log \frac{l}{m} + \frac{m}{\pi} \log\left(\frac{m}{l-m}\right).$$

$$X/l = \frac{1}{\pi} \left\{ \frac{m}{l-m} \log \frac{l}{m} + \frac{m}{l} \log \frac{m}{l-m} \right\}. \quad \dots \quad (68)$$

For calculating the complete distribution, t must be eliminated from equations (62) and (63), so that the co-ordinates $(x+iy)$ of the z plane may be obtained in terms of those $(u+iv)$ of the w plane.

Thus from (62)

$$t = 1 - e^{u\pi/l} \{ \cos(v\pi/l) + i \sin(v\pi/l) \}, \quad . \quad . \quad (69)$$

while from (62) and (63)

$$x+iy = \frac{l-m}{l} (u+iv) + \frac{m}{\pi} \log \left[1 + \frac{(l-m) \{ 1 - e^{u\pi/l} \{ \cos(v\pi/l) + i \sin(v\pi/l) \} \}}{m} \right]. \quad (70)$$

Hence

$$x = \frac{l-m}{l} \cdot u + \frac{m}{2\pi} \log(A^2 + B^2), \quad . \quad . \quad . \quad (71)$$

$$y = \frac{l-m}{l} \cdot v + \frac{m}{\pi} \tan^{-1}(B/A), \quad . \quad . \quad . \quad (72)$$

where

$$A = \frac{l - (l-m)e^{u\pi/l} \cos(v\pi/l)}{m}, \quad . \quad . \quad . \quad (73)$$

$$B = \frac{-(l-m)e^{u\pi/l} \sin(v\pi/l)}{m} \quad . \quad . \quad . \quad (74)$$

From these relations the coordinates of the points of intersection of the isothermals $v = 0, l/4, l/2, 3l/4$, and l , with the flow lines $u = 0, l/4, l/2 \dots$ have been calculated, and are shown in fig. 8. In order to show in greater detail the nature of the flow near the sharp edge, portions of the isothermals $v = l/8$ and $l/16$ and the flow line $u = 3l/8$ have also been calculated. It will be observed that at a comparatively short distance from the edge in either direction (see flow lines $u = \pm 5l/4$) the flow becomes practically normal.

Comparison of Boundary Distribution for T-Ribs of Finite and Infinite Widths.

It is clear from the preceding section that the general distribution of flow lines and isothermals will be very similar in these cases, unless the width of the rib is small. An exact comparison of the distribution along the boundaries can however be made, that for the rib of infinite width being of course covered by the preceding section, and that for the

rib of finite width being deducible from equations (27) and (55). Thus from (27), since $P = l/\pi$ and $t = \text{sn}^2 \zeta$, we have

$$\text{sn } \zeta = \frac{\tanh(w\pi/2l)}{k \text{ sn } \alpha},$$

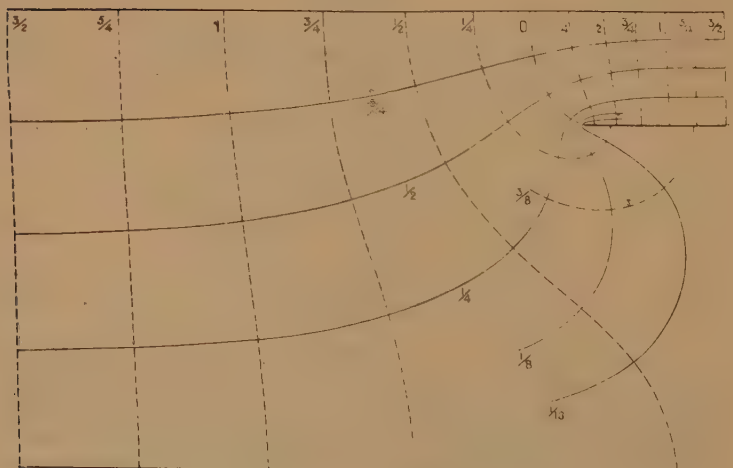
and the following deductions can be made as to boundary distribution:—

(a) *Lower Isothermal Boundary—along OE and EA* (fig. 6).

Here $v = 0$ and $y = 0$, so that

$$x = \frac{l}{\pi} \log \frac{\Theta(\zeta + a)}{\Theta(\zeta - a)}, \quad \dots \dots \dots (75)$$

Fig. 8



where

$$\text{sn } \zeta = \frac{\tanh(u\pi/2l)}{k \text{ sn } \alpha} \quad \dots \dots \dots (76)$$

(b) *Lower Isothermal Boundary—along BC.*

Here $v = 0$, and the variable ζ is replaced by ϕ , where $\zeta = K + iK' - \phi$, so that

$$x + iy = \frac{l}{\pi} \log \left\{ \frac{\text{cn}(a - \phi) \Theta(a - \phi)}{\text{cn}(\phi + a) \Theta(\phi + a)} \right\} + im, \quad \dots \dots \dots (77)$$

where

$$\frac{\text{dn } \phi}{\text{cn } \phi} = \frac{\tanh(u\pi/2l)}{\text{sn } \alpha} \quad \dots \dots \dots (78)$$

Calculation of "Added Length."

The calculation is made in a similar manner to that adopted in the preceding cases. From (56) we obtain directly the value r (or $90 a/K$) required to give the chosen

TABLE II.

Comparison of Boundary Distribution of Flow Lines for T-Ribs of Finite and Infinite Widths, each of depth $m = 3l/4$.

n/l .	$u/$	x/l (origin E, direction EO negative) along		
		CD.	EO.	BC.
0.280	-1.0	-0.180	-0.184	—
∞		-0.179	-0.184	—
0.280	-0.5	-0.045	-0.068	—
∞		-0.044	-0.069	—
0.280	0	+0.120	0	—
∞		+0.122	0	—
0.280	+0.5	+0.378	—	—(on AB)
∞		+0.382	—	-0.187
0.280	+0.535	+0.402	—	-0.280 (B)
∞		+0.406	—	-0.053
0.280	+0.75	+0.559	—	+0.354
∞		+0.564	—	+0.374
0.280	+1.0	+0.769	—	+0.680
∞		+0.776	—	+0.692

ratio of m/l . b is then computed from (53), and n/l and X/l from (57) and (59) respectively. A series of values for the case of $m = 3l/4$ is given in fig. 4 (see curve marked T3/4), and it will be observed the "added length" shows a decrease with increase of the value of n , the final value as given by equation (68) being however reached very rapidly.

The case of $m = l/2$ admits of algebraic treatment, since it is obtained by putting $a = K/2$ or $r = 45^\circ$.

Thus, substituting the following values in (53),

$$\begin{aligned}\operatorname{sn}(K/2) &= 1/\sqrt{1+k'}, & \operatorname{cn}(K/2) &= \sqrt{k'/(1+k')}, \\ \operatorname{dn}(K/2) &= \sqrt{k'}, & Z(K/2) &= (1-k')/2.\end{aligned}$$

We find that $b = K/2$, while from (57)

$$\frac{n}{l} = \frac{1}{\pi} \log \frac{\Theta(K)}{\Theta(0)} = \frac{1}{\pi} \log \frac{1}{\sqrt{k'}} \quad \dots \quad (75)$$

Hence, from (59),

$$\begin{aligned}\frac{X}{l} &= \frac{1}{\pi} \log \frac{2}{\sqrt{k'}} - \frac{1}{\pi} \log \frac{1}{\sqrt{k'}} \\ &= \frac{1}{\pi} \log 2; \quad \dots \quad (76)\end{aligned}$$

so that we have the curious result that, for the case of $m = l/2$, the "added length" is a constant independent of the value of n . This result is confirmed by the values given by equations (30) and (68) for the marginal cases of $n = 0$ and ∞ .

Comparison of "Added Lengths" of Buttress, T-Rib, and thin Rib.

The second of these cases differs from the first in that it has the additional re-entrant portion of sides EA, AB (see fig. 6). This re-entrant portion obviously produces a decrease in the total heat-flow, the precise magnitude of which for the two cases of $m = l/2$ and $3l/4$ is indicated by the distance apart of the B and T curves on fig. 4. The calculation of the complete curves, like those shown on fig. 4, for a series of values of m/l would be very laborious; but since the final value of the "added length" in either case is very nearly attained for comparatively small values of n/l , a close idea of the values in the two cases may be obtained by using equations (37) and (68), which give these final values, *i.e.* for $n/l = \infty$.

A series of values has accordingly been calculated on this basis, and is given in Table III., together with those obtained from equation (30) for the single thin rib which is the limiting form of both buttress and T-rib when $n/l = 0$.

It will be observed that, for values of m/l up to 0.5, the added length for the T-rib falls intermediate between those for the other two cases, while for greater values of m/l it is

less than for the others, being in the limit when $m = l$, one-half of the added length for either of the other cases.

TABLE III.

Comparison of "Added Lengths" of Buttress, T-Rib, and thin Rib.

m/l .	Values of X/l for		
	$n/l = 0$.	$n/l = \infty$.	
	Thin rib.	Buttress.	T-rib.
0.1	0.0079	0.0122	0.0115
0.25	0.050	0.065	0.060
0.5	0.221	0.250	0.221
0.75	0.611	0.650	0.537
0.9	1.181	1.222	0.929
$1 - \frac{1}{p}$ ($p \rightarrow \infty$)	$\frac{2}{\pi} \log p$	$\frac{2}{\pi} \log p^*$	$\frac{1}{\pi} \log p$

* Lees, Phil. Mag. xvi. p. 739 (1908).

GENERAL NOTE ON SIMILAR CASES.

The cases dealt with above fall under the general head of polygons, the boundaries of which consist of two isothermals, at different temperatures, together with two flow lines joining the ends of these isothermals. The method of solution consists in transforming, through an intermediate plane, the polygon into a rectangle, the opposite sides of which form the pair of isothermals or flow lines, as the case may be, and in which the complete isothermal and flow-line distribution is therefore rectilinear. According to the boundary conditions, the final rectangle will be finite, or semi-infinite or infinite along one axis, or infinite along one axis and semi-infinite along the other. The first case occurs when none of the two boundary isothermals or two boundary flow lines is situated entirely at infinity, while the other three cases occur respectively when one, a pair, or three of the boundary

isothermals or flow lines are so situated. There is also the special case where a boundary flow line or isothermal is of zero length, *e.g.* a point source. The rectangle appropriate to this case would be semi-infinite, the point isothermal or flow line of the z plane becoming the side of the rectangle at infinity. Examples of transformations from the w to the t plane applicable to the first three cases described above are equations (7), (27), and (62). It will be seen that the finite rectangle involves the first type of elliptic integral and the other cases simpler functions. In the fourth case, which is infinite along one axis and semi-infinite along the other, the rectangle becomes in fact one-half of the intermediate (t) plane, so that the final transformation to the w plane is rendered superfluous.

The transformation from the z to the t plane is, of course, more diverse in type and, as a general rule, more difficult of manipulation than that from the w to the t plane. It may, however, be pointed out that the cases of the buttress, recess,

Fig. 9.



and T-rib treated above have the common feature of a z -plane transformation involving in part the third type of elliptic integral, and that this fact, together with the common w -plane transformation, has resulted in the first term in the expression for the "added length" being identical in the three cases (see equations (29), (49), and (59)).

Attention may also be drawn to the method, followed where appropriate throughout this paper, of deriving the z -plane transformation from a diagram obtained by dividing the figure by a line or lines of symmetry instead of using the complete original form. While this method of treatment has been of no immediate advantage in these particular instances, there are problems in which it results in considerable simplification, and in any event it serves to show the inter-connexion between cases apparently dissimilar. Thus, as already mentioned, Carter found it convenient, in dealing with the problem illustrated in fig. 9, to make use of the z -plane transformation applicable to fig. 1 (*c*), both these

figures giving the contour of fig. 5 on insertion of lines of symmetry. The boundary distribution of flow lines and isothermals would not be identical in the two cases, but this would not affect the z -plane transformation, but merely the second and simpler transformation from t to w plane

In a similar way the z -plane transformation applicable to fig. 5 will also apply to figs. 10 (a) and (b), in the latter case

Fig. 10.



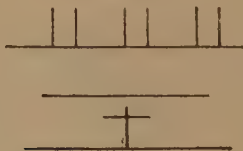
with the omission of either of the short upright lines if desired. Examples of problems covered by the z -plane transformation of fig. 3 are shown in fig. 11. Of these,

Fig. 11.



(a) and (b) are understood to have the second isothermal boundary at infinity, while in the case of (b) the alternate upright lines may be omitted if desired. Fig. 12 indicates problems governed by the z -plane transformation of fig. 6.

Fig. 12.



Finally, it may be pointed out that, since the complete system of the isothermals in any case is interchangeable with that of the flow lines, the solution of any problem gives that of the cognate problem obtained by effecting this interchange.

LIV. *Experiments on a Ferromagnetic Compound of Manganese and Arsenic.* By L. F. BATES, B.Sc., Ph.D.,
Lecturer in Physics, University College, London*.

IN an examination of the thermal and magnetic properties of a ferromagnetic substance consisting of equal parts of manganese and arsenic, the writer† found that the specific heat of the substance rose from a value of 0.12 in the neighbourhood of 28° C. to a value of about 0.14 at 36° C., thence with increasing rapidity to a value of about 1.0 at 42° C., and then fell rapidly to a value of 0.13 at 45° C. The maximum value of the specific heat was found at 42.2° C. It was also found that the rate of decrease of the intensity of magnetization with rise in temperature, dI/dT , was a maximum at 42.2° C., whereas dI^2/dT was a maximum at 41.5° C. According to the Weiss theory of ferromagnetism, the specific heat of a ferromagnetic substance should exhibit a maximum at the temperature at which dI^2/dT is a maximum.

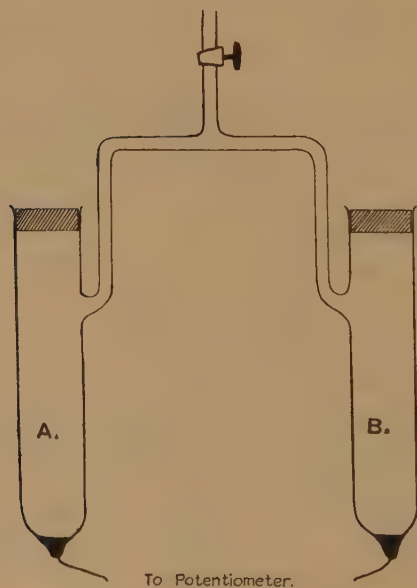
It was therefore hoped that further information would be obtained from experiments carried out on the following lines. A glass apparatus of the form shown in fig. 1 was constructed. Very short platinum wires were sealed through the lower ends of the vertical tubes. Some of the substance was placed in these tubes, so that the platinum leads were completely covered. The apparatus was then filled with a solution containing 40 c.c. of decinormal hydrochloric acid and 60 c.c. of distilled water, in which was dissolved 4.44 gm. of manganese chloride. A cork was fitted to each tube, and through that in tube A there passed a thermometer whose bulb rested in contact with the substance. The tube A was placed in a glass vessel containing paraffin and provided with an electrical heater, stirrer, and thermometer, whilst the tube B was placed in a glass vessel and surrounded with ice. The potential difference between the two electrodes was frequently determined as the temperature of the tube A was slowly raised. Curve *a* (fig. 2) shows a typical set of determinations, obtained after the substance had been in contact with the solution for some days. It will be observed that as the temperature rose the electrode A was at first positive with respect to the electrode

* Communicated by Prof. Alfred W. Porter, F.R.S.

† Bates, Proc. Roy. Soc. A, cxvii. p. 680 (1928).

B, the potential difference gradually reached a maximum and then decreased slowly, until in the neighbourhood of 40°C . it began suddenly to decrease, attained a minimum and negative value and again increased. The phenomenon was not a simple one, for the shape of the curve depended on the rate at which the temperature was raised during the set of observations. Thus curve *b* (fig. 2) shows the type of curve which was obtained when the temperature of the tube A was raised about four to five times as quickly

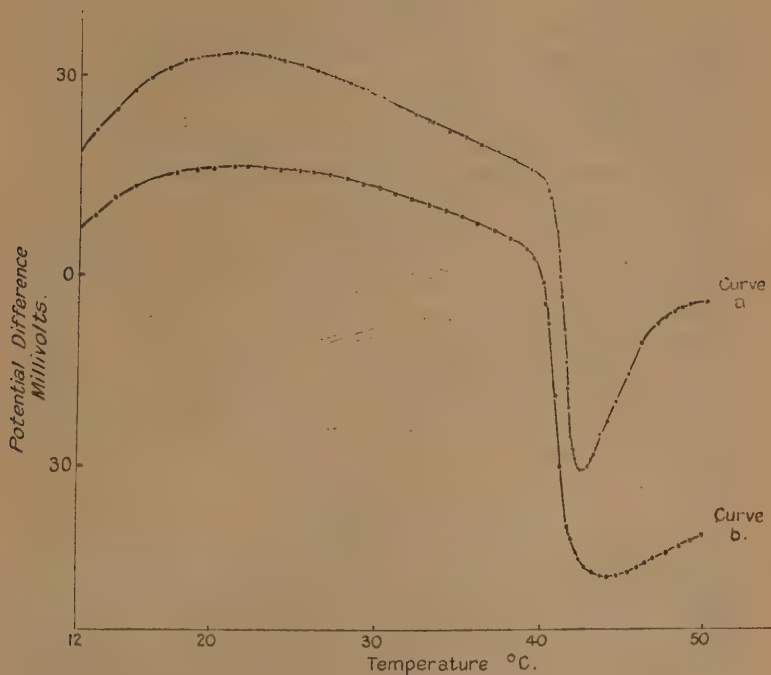
Fig. 1.



as in curve *a* (fig. 2). Curves of an intermediate form were obtained when the rate of rise of temperature was between the rates for curves *a* and *b*. Some further information was obtained from a set of observations made as follows. The temperature of tube A was raised slowly to 21°C ., and then maintained constant for forty-five minutes. During this interval of time the electrode A became considerably less positive. The temperature was then slowly raised to 29°C ., and the potential at the end of an equal interval of time again showed a considerable change in the same direction. This behaviour continued at each stationary temperature until a temperature of approximately 41°C . was reached,

where, during the forty-five minutes for which the temperature was maintained constant, the potential of the electrode A became considerably more positive. Similar changes were always observed when the temperature was above 41°C . These changes were no doubt due to polarization phenomena. When the temperature of the tube A was raised more and more quickly, the polarization phenomena would be less and less completely established, and this

Fig. 2.



Note.—The ordinates of curve *b* have been displaced downwards by 30 millivolts.

would contribute a great deal to the differences between curves *a* and *b* (fig. 2). Now the substance exhibits pronounced temperature hysteresis, the ferromagnetic properties disappearing completely at 45°C . when the temperature is raised from 0°C ., and reappearing at 34°C . when the substance is cooled. The behaviour of the potential difference was therefore followed when the tube A was initially heated

to 54° C. and then allowed to cool. At 34° C. there was a sudden change in the potential of the electrode A, the electrode becoming more negative and reaching its most negative value at about 30° C., after which it became more positive. The changes, however, were very much less marked than those previously described. Such cooling experiments were difficult to carry out in a satisfactory manner, and the results were very difficult to interpret.

Discussion.

The above curves indicate in a striking manner the existence of a critical point in the neighbourhood of 42° C. Polarization phenomena, of course, make the interpretation of the results somewhat difficult. Let us assume, however, that we are dealing with a reversible electrode, and that q is the amount of heat liberated when an amount of the substance carrying unit charge of electricity goes into solution. Then the relation $T(d^2E/dT^2) = -dq/dT$ should be obeyed. Included in the quantity q is the energy of demagnetization, and thus dq/dT must contain the corresponding rate of change. According to Weiss this is directly proportional to dI^2/dT . Consequently, on this theory, $T(d^2E/dT^2)$ should exhibit a maximum at the temperature at which the value of dI^2/dT is a maximum. Naturally, this assumes that no complicated chemical changes obscure the maximum. The above curves show that a maximum value of $T(d^2E/dT^2)$ occurs just about 42° C. In the experiments on specific heat the maximum value of the specific heat was found at 42.2° C., whilst dI^2/dT was a maximum at 41.5° C. Since the substance was investigated in the form of a powder, it was conceivable that a lag in the apparatus used for the determination of the specific heat, or poor thermal conductivity of the substance, was responsible for the difference between the experimental and the theoretical temperatures of the maximum specific heat. The present results appear to indicate that the difference is a real one. It may be mentioned here that the experiments of Sucksmith and Potter* show that the specific heat may behave in a very different manner from that predicted by the Weiss theory. Their experiments were made at high temperatures, and experimental difficulties prevented them from finding whether the maximum

* Sucksmith & Potter, Proc. Roy. Soc. cxii, p. 157 (1926).

value of dI^2/dT actually coincided with that of the maximum value of the specific heat in their experiments. It has been suggested * that the atoms of ferromagnetic metals are associated in definite groups containing ions of different valencies which possess the same magnetic moments as the ions in solid salts and paramagnetic solutions, although it now appears very doubtful † that the magnetic carriers in paramagnetic solutions are simple ions. We can only say that the above results do not oppose this suggestion. On the theory of ferromagnetism recently put forward by Honda ‡ the loss of ferromagnetism would result from a re-orientation of the nuclei of the manganese and arsenic atoms in such a way that the resultant angular momentum of the group of atoms was no longer negligibly small. Presumably the energy supplied with rise in temperature would cause destruction or modification of the group so that the individual nuclei would be free to rotate, and the resultant angular momentum of the group would be too large to permit it to be orientated by an external magnetic field. Thus on Honda's theory the rate of change of the intensity of magnetization should correspond with the rate of supply of heat with rise in temperature; and this is what was shown in the previous experiments. However, it appears that the Honda theory would require the absence of the gyromagnetic phenomena which have been firmly established by the experiments of a large number of workers.

Summary.

Experiments are described which show the behaviour of the potential difference between a ferromagnetic substance, consisting of equal parts of manganese and arsenic, and a solution containing a manganese ion. Pronounced changes occur as the substance passes through its magnetic critical temperature.

It gives me much pleasure to acknowledge the kind interest with which Professor A. W. Porter, F.R.S., followed the course of this work.

* Stoner, Proc. Leeds Phil. Soc., Jan. 1926.

† Joos, *Annalen der Phys.* lxxxv. p. 641 (1928).

‡ Honda, *Zeit. für. Phys.* xlvii. p. 691 (1928).

LVI. *Notices respecting New Books.*

Cremona Transformations. By HILDA P. HUDSON, Sc.D. (Cambridge University Press. Price 42s. net.)

THIS volume gives a connected and comprehensive account of Cremona transformations in plane and space, with their applications to problems in higher geometry, especially to the resolution of singular points of curves and surfaces and the study of contact theories. Miss Hudson's researches, on both plane and space transformations, extend over a number of years, and her contributions to this branch of mathematics are well known. The bibliography shows in some measure the wealth of material largely incorporated in this work. Reference is made to Coble's report on Cremona transformations, and applications to algebra, geometry, and modular functions. All the important results of modern investigators are here collected and classified, and in this way valuable service has been rendered to workers in this special branch of geometry. An interesting chapter is devoted to the history and literature of the subject and attention drawn to problems which await solution. This volume is a worthy companion of the mathematical treatises already published by the University Press.

Theory of Vibrating Systems and Sound. By IRVING B. CRANDALL, Ph.D. (Macmillan & Co., St. Martin's St., London. Price 20s. net.)

Dr. CRANDALL's book is largely based upon the lectures given by him at the Massachusetts Institute of Technology, and presents, in the main, a mathematical treatment of the subject of Sound. Bessel functions of various kinds, with real, imaginary, and complex arguments, are in evidence in the study of vibrations of circular membranes, cylindrical tubes, vibrating strings, and the resistance coefficients for conduits. The chapter on radiation and transmission problems deals with the end corrections for a tube and the study of conical and exponential horns. The investigations of P. E. and W. B. Sabine in Architectural Acoustics are largely incorporated in the final chapter. Problems on the subject matter are given at the end of the chapters.

To those interested in acoustic research, the appendix giving the recent developments, both experimental and technical, will be helpful. Reference is made to original papers contributed during the last four or five years and include such diverse subjects as telephones, resonators, and transmitters, and the numerous devices introduced during the war for submarine signalling, sound-ranging, and direction-finding.

The Acoustics of Buildings. By A. H. DAVIS, D.Sc., and G. W. C. KAYE, D.Sc. (George Bell & Sons, York House, Portugal St., London. Price 15s. net.)

THIS volume on the behaviour of sound in buildings deals with the technical aspect of the subject. The introductory chapter on the production and measurement of sound is devoted to the analysis of sounds and the characteristics of speech, and describes some of the modern instruments for the measurement of sound intensity—Rayleigh's disk, the hot-wire microphone of W. S. Tucker, and the electrostatic microphone of Wentz. The practical applications of acoustic theory are considered under various headings; the reflecting characteristics of boundaries and the method adopted in their study—some excellent photographs illustrate the sound-pulse and ripple-tank methods; reverberation, with the methods for the measurement of absorption coefficients and the correctness of defects due to echoes and reverberation. The researches of W. C. Sabine and his successors in the Jefferson Physical Laboratory, and, within the last ten years, in the Sabine Laboratory, Geneva, Illinois, and those of F. R. Watson, investigated in the National Physical Laboratory, are reviewed in the section on the measurement of sound transmission. An interesting chapter on special types of auditorium traces the development of modern practice from the open-air theatre, Greek and Roman, and discusses the acoustic properties of buildings both in England and America. By bringing together many of the most recent results of applied acoustics, the authors have placed workers in this field under a considerable obligation.

Foundations of Euclidean Geometry. By H. G. FORDER, B.A. (Cambridge University Press. Price 25s. net.)

MR. FORDER has successfully accomplished the task of erecting Euclidean Geometry on a sound yet narrow basis and has provided a connected and "rigorous" account of modern investigations, with occasional references to non-Euclidean geometries. Axioms of order and congruence are first considered, circle and parallel axioms and the theorems of Pappus and Desargues. Then follow chapters on the Analysis Situs of plane polygons and polyhedra, the theory of areas and of volumes of polyhedra. The last two chapters are devoted to Pieri's set of axioms ("La Geometria Elementare") and to the discussion of the angle-sum of a triangle, with the related theory of non-Euclidean areas. References are also given to other investigations into the foundations of Geometry which differ from that given by the author, in particular the work of Weyl and Veblen. The book closes with useful lists of symbols and axioms of order, congruence, etc. The author rightly claims that a careful study of the volume should result in a general improvement of Geometrical teaching.

Practical Physics. By T. G. BEDFORD, M.A. (Longmans, Green & Co., 39 Paternoster Row, London. Price 10s. 6d. net.)

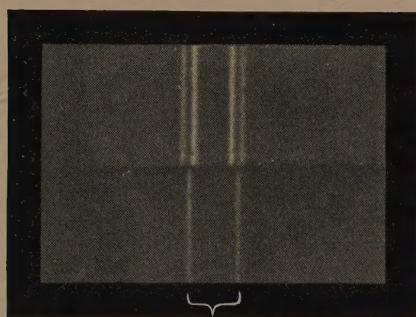
MR. BEDFORD'S wide and varied experience as Demonstrator in the Cavendish Laboratory has been drawn upon in the compilation of this excellent text-book of practical physics—a modern “Glazebrook and Shaw.” The large number of experiments described cover the elementary portions of the subject, properties of matter, heat, light, sound, magnetism, and electricity; many of the experiments require only the simplest kind of apparatus, but even with this slender equipment a considerable degree of accuracy can be obtained. Other experiments of a more advanced character given in the additional exercises at the end of each chapter are intended for those who have completed the preliminary course. Students who have mastered the book will be well fitted to undertake the experimental work in elasticity, optics, etc. in Dr. Searle's well-known volumes.

Electric Rectifiers and Valves. By Prof. A. GÜNTHERSCHULZE. Translated by N. A. DE BRUYNE, B.A. (Chapman & Hall, 11 Henrietta St., London. Price 15s. net.)

MR. DE BRUYNE'S book is both a translation and revision of Prof Güntherschulze's “Elektrische Gleichrichter und Ventile.” The first part of the book, the physical theory section, sets out the principles of valve-action and brings under review the introductory study of atomic structure, electric conduction in gases, electron production (photo-electric, thermionic, and glow), arc and spark discharges, and electrolytic rectifiers. The second part, technical section, opens with a chapter on the mathematical theory of valves, giving in particular the equations for various arrangements of valve circuits. Mechanical and electrolytic rectifiers are briefly noticed, followed by an account of the Wehnelt rectifier and the different types of mercury arc rectifiers. A table is given showing the useful ranges of different kinds of rectifiers. The publishers have rendered good service by adding this volume to their series of technical manuals.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

FIG. 1.



O λ 5577.341.
Two orders.

FIG. 2.



Ne λ 5852.
Two orders.

